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Heat Transmission in Rotary Kilns.—X.
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(207)   Part IX dealt with the effect of wide changes in the kiln diameter, and in the charge per cent. on the rate of heat transmission per unit of volume and per unit of surface in the decomposition zone.   The results obtained were used to ascertain the advantage of a well-known type of kiln provided with a decomposition zone extra large in diameter.   It is now proposed to deal in a similar manner with the drying zone.   The representative stages selected are Nos. (2) and (5) in which the first and last quarters respectively of the slurry moisture are evaporated.

The heat transmission of the plain kiln, without chains or slurry lifters, is first considered.   In each stage the inquiry relates to (a) The effect of varying the kiln diameter from 2 ft. to 15 ft. when the charge remains constant at 6 per cent. and (b) The effect of varying the charge from 5 per cent. to 20 per cent. when the area of the gasway remains constant.   Working conditions such as clinker output, coal consumption, and the gas composition, velocity, and temperature in each stage are again assumed to be similar to those of the 400 ft. kiln.

(208) It may be useful at this stage to refer generally to the method of calculation adopted.   Each stage represents a short length of the kiln.   In the combustion zone the flame temperature is taken at 2,450 deg. F. throughout.   In each of the remaining stages the average gas temperature is calculated from the preliminary data.   The average material temperature in each stage is fixed in the first instance.   The lining temperature is found by trial; it must be sufficient to pass on to the material the heat which it receives from the flame or gas.   In the drying zone the fluctuation of the lining surface temperature during each revolution is small enough to be neglected; in the remaining stages it is taken into account.

(209) Fig. 38 shows in cross section a kiln containing a 6 per cent. charge. The flame or gas gives up heat in two ways, (a) to the material chord AB and

(b) to the upper lining arc ADB. The kiln lining distributes the heat which it receives in three ways, (c) by radiation, through the flame or gas, to the chord AB, (d) by radiation or conduction to the material arc ACB as the lining passes under, and (e) by shell radiation.

(210) When the rate of heat transfer from the flame or gas to the kiln lining is rapid, and that from the lining to the material relatively slow, a 6 per cent. charge will be too small, but when the rate of heat transfer from the gas to the lining is slow and that from the lining to the material rapid a 6 per cent. charge is suitable. Stage (10) is an example of the former and stage (2) of the latter.

If the charge in the kiln is increased, the lining temperature falls, quickly in stage (10), for instance, but slowly in stage (2). The inquiry now proceeds in accordance with para. (207a).

Stage (5).—Diameter Variable, Charge 6 per cent.

(211) The preliminary figures are·taken mainly from Table XIX in Part VI, the average gas temperature being 1,993 deg. F., the gas velocity 39.3 ft. per second, and the value of H_{con} 22. Since charges up to 20 per cent. are now
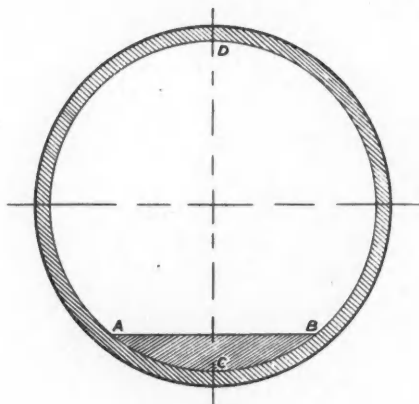

Fig. 38.

considered the gas velocity is calculated on the area in cross section after the space occupied by the charge has been deducted. This area is termed the gasway. An equivalent ring 1 ft. wide has been taken at the centre of the stage, and the heat transmission per minute to the material worked out for kiln diameters of 2, 4, 6, 8, 11, and 15 ft. with a 6 per cent. charge. On dividing by πD (where D is the corresponding diameter inside the lining in feet), the heat transmission per square foot of lining surface area per minute is obtained, and on dividing by $\frac{\pi}{4} D^2$ the heat transmission per cubic foot of volume per minute is found.

(212) The resulting figures are shown on Fig. 39, where the base-line represents the kiln diameter in feet, curve AA gives for any diameter the heat
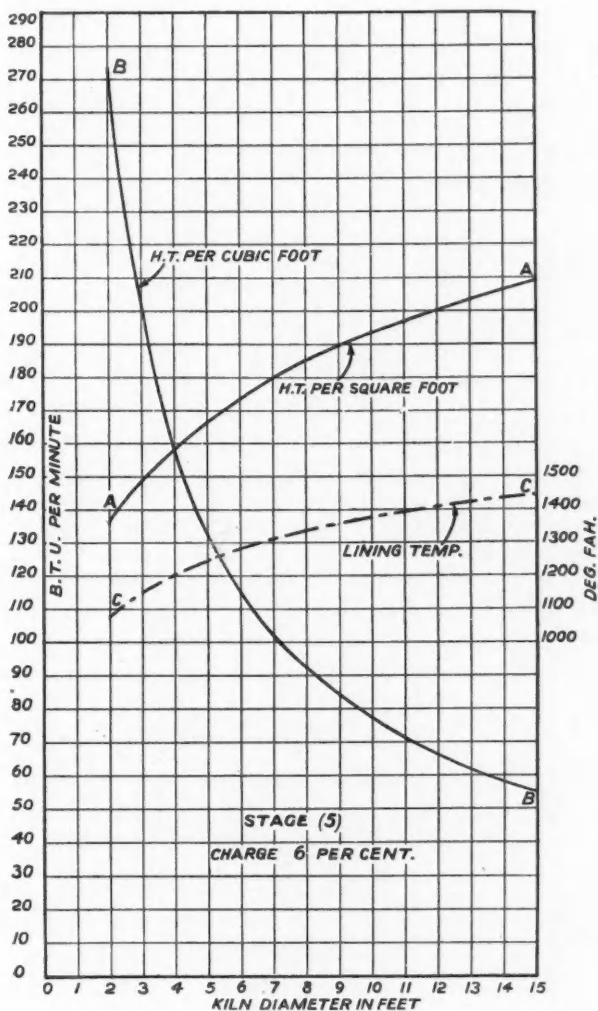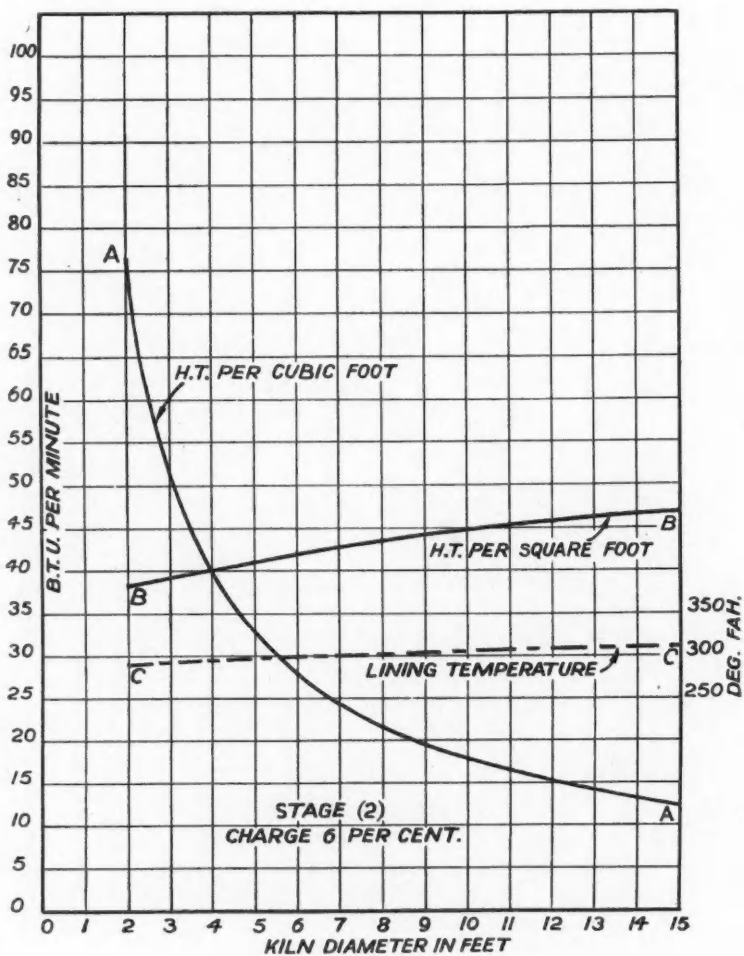
Fig. 39.

Fig. 40.

transmitted per square foot of surface area per minute, and curve *BB* shows the heat transmitted per cubic foot of volume per minute. As in the case of stage (10) the rate of heat transmission to the material (or in other words the kiln output) has no real relation to the volume of the kiln. Curve *AA* shows that the rate of heat transfer per square foot of surface area increases rather rapidly with increase of diameter. The average lining temperature (for the circle) is shown by curve *CC* to the scale on the right.

Stage (2).—Diameter Variable, Charge 6 per cent.

(213) Proceeding in accordance with para. (207a), the heat transmission in stage (2) is next examined. The preliminary figures are again taken mainly from Table XIX, Part VI, the average gas temperature being 811 deg. F., the gas velocity 25.2 ft. per second, and the value of H_{con} 91.

The heat transmission per foot run of kiln per minute has been worked out for kiln diameters of 2, 4, 6, 8, 11, and 15 ft., and Fig. 40 is based on the results obtained. Curve *AA* shows the heat transmitted in B.T.U. per minute per cubic foot of volume, and curve *BB* shows the heat transmission per square foot of lining surface area. The average lining temperature (for circle) is shown by curve *CC*.

Stage (5).—Gasway Constant, Charge Variable.

(214) The inquiry proceeds in accordance with para. (207b), and it is now proposed to determine the rate of heat transfer in stage (5) when the charge varies from 5 to 20 per cent. The kiln diameter is taken at 8.16 ft. for the 5 per cent. charge rising to 8.89 ft. for the 20 per cent. charge, the small increase of diameter being required to keep the area of the gasway constant. At the 6 per cent. charge the stage diameter is the same as it was in the 400-ft. kiln. The preliminary figures are those referred to in para. (211.)

The heat transmission per foot run of kiln per minute has been worked out for charges of 5, 8, 13, and 20 per cent. respectively. The kiln is assumed to make one revolution per minute in all cases, the slope being altered to give the charge required. The general result is shown on the upper part of Fig. 41. The base-line represents the charge per cent., curve *AA* shows for any charge the rate of heat transmission per square foot of lining surface area per minute, and curve *BB* gives the average lining temperature (for circle).

Stage (2).—Gasway Constant, Charge Variable.

(215) The preliminary figures are those referred to in para. (213). The heat transmission in B.T.U. per foot run of kiln per minute has been worked out for charges of 5, 8, 13, and 20 per cent. as before. The diameter for the 5 per cent. charge was 8.71 ft. rising to 9.5 ft. for the 20 per cent. charge, the area of the gasway being thus maintained constant. At the 8 per cent. charge the stage diameter is the same as it was in the 400-ft. kiln.

On dividing the heat transmission per foot run by πD, the heat transfer in B.T.U. per square foot of lining surface area per minute is obtained ; the result is shown on the lower part of Fig. 41 and by curve *CC*. The average lining tem-
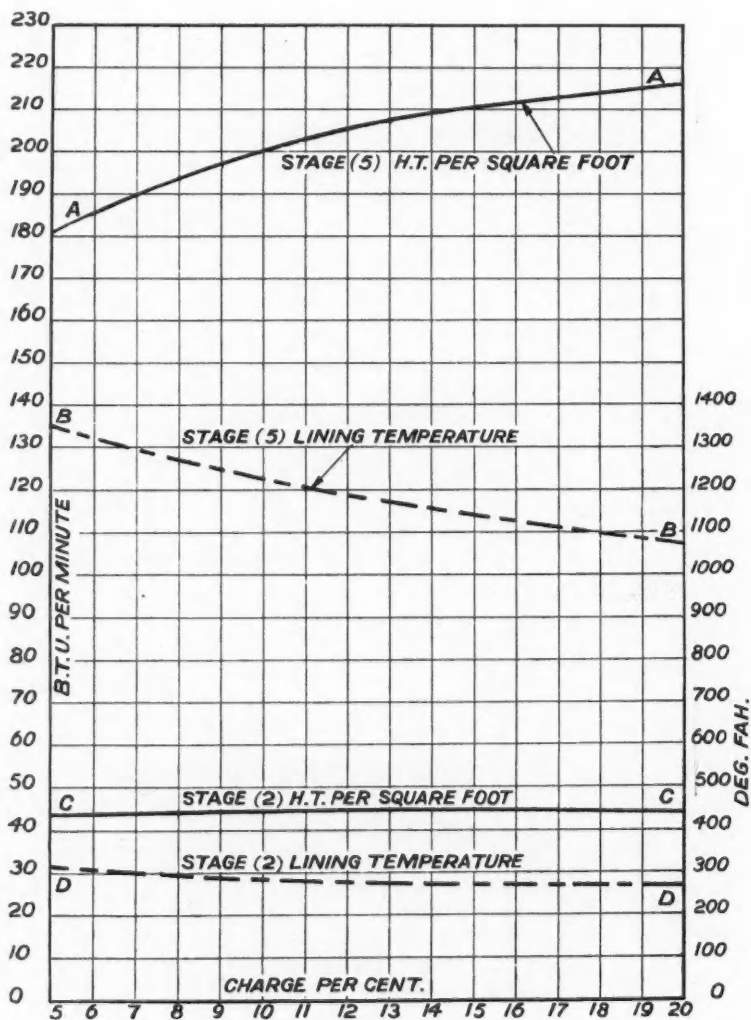
Fig. 41.

perature (for circle) is shown by curve *DD*.   It is seen that in stage (2) a relatively large charge does not increase the rate of heat transfer.

Arc and Chord Lengths for Various Charges.

(216) Table XXXI will be found useful at this stage.   For charges between 3 per cent. and 26 per cent. it gives the radial depth of the charge at the centre expressed as a percentage of the kiln diameter inside the lining, also the lengths

TABLE XXXI.—Showing the Charge Dimensions for Charges of 3 to 26 per cent.

Charge per cent.	Depth of charge per cent. D	Per cent. circumference			Charge per cent.	Depth of charge per cent. D	Per cent. circumference		
		Upper arc	Lower arc	Chord			Upper arc	Lower arc	Chord
3	6·9	83·07	16·93	16·14	15	20·7	69·93	30·07	25·80
4	8·4	81·28	18·72	17·66	16	21·7	69·15	30·85	26·25
5	9·7	79·83	20·17	18·85	17	22·6	68·46	31·54	26·63
6	11·0	78·48	21·52	19·92	18	23·6	67·70	32·30	27·04
7	12·2	77·29	22·71	20·84	19	24·5	67·04	32·96	27·38
8	13·4	76·14	23·86	21·69	20	25·4	66·37	33·63	27·71
9	14·6	75·04	24·96	22·49	21	26·3	65·72	34·28	28·03
10	15·6	74·15	25·85	23·10	22	27·2	65·07	34·93	28·32
11	16·7	73·20	26·80	23·74	23	28·1	64·44	35·56	28·62
12	17·8	72·27	27·73	24·36	24	28·9	63·87	36·13	28·86
13	18·8	71·44	28·56	24·88	25	29·8	63·24	36·76	29·12
14	19·8	70·64	29·36	25·38	26	30·7	62·61	37·39	29·36

of the upper lining arc, the lower lining arc, and the material chord each expressed as a percentage of the lining circumference.

Summary of Results for Plain Kiln.

(217) When the kiln diameter is assumed to vary with a constant charge of 6 per cent., Figs. 32, 39 and 40 show for stages (10), (5), and (2) the rate of heat transfer from the kiln gases to the material per minute per cubic foot of volume and per square foot of lining surface area.   As the diameter increases from 8 ft. to 15 ft. (which is the range of interest in practice) the increase in the rate of heat transfer per square foot of lining surface is 10.8 per cent. in stage (10), 13 per cent. in stage (5), and 8 per cent. in stage (2).   In stage (10), and to a less degree in stage (5), the rate of increase is kept down by the high lining temperature due to the small charge.

(218) When the charge is assumed to vary, keeping the diameter constant or nearly so, the effect on the rate of heat transfer per square foot of lining surface area per minute in stages (10), (5), and (2) is shown by Figs. 33 and 41.   The chief results are summarised in Table XXXII.

TABLE XXXII.—RELATION BETWEEN CHARGE PER CENT. AND RATE OF HEAT
TRANSFER IN STAGES (10), (5) AND (2).

	Stage (10).	Stage (5).	Stage (2).
(a) Average kiln diameter .. .. .. (ft.)	10·2	8·52	9·10
Relative rate of heat } (b) at 5 per cent. charge ..	100	100	100
transmission } (c) at 20 per cent. charge	133	120	101
Unit rate of heat { (d) Flame or gas to upper arc	82	14	5
transmission } (e) Lower arc to material	47	22	91

Lines (b) and (c) show the relative increase in the heat transmitted to the material per square foot of lining surface per minute as the charge is increased from 5 to 20 per cent. It is seen that a relatively large charge is advantageous in stage (10) and to a smaller extent in stage (5), but is of little or no advantage in stage (2).

Lines (d) and (e) give the average rates of heat transmission to and from the kiln lining expressed in B.T.U. per square foot per hour per deg. Fah. temperature difference. Para. (210) should be again read in this connection.

Relation Between the Rate of Heat Transmission and the Charge per cent. when Chains are Used.

(219) In stages (1), (2), and (3) when chains are used it is not necessary to consider the effect of varying the kiln diameter with a constant charge per cent. since it is desirable to keep the diameter relatively small and the gas velocity past the chains relatively high in order to increase the rate of heat transmission. In stages (10) and (11) the effect of the gas velocity on the rate of heat transmission is small, hence the kiln diameter can be fixed by other considerations. It remains to consider the effect of varying the charge per cent.

(220) A cross section through the drying zone of a rotary kiln provided with chains is shown in Fig. 42. Charges of 5, 8, 13 and 20 per cent. are drawn to scale. The chains are suspended at one end in rows parallel to the axis of the kiln, and on the lining surface in this instance the rows are 20 in. pitch. The diagram also shows the path through the gasway of the lower end of the chain for chain lengths of 0.5 D, 0.6 D, and 0.7 D respectively where D is the diameter inside the kiln lining. The rate of heat transmission has been worked out in stages (1), (2) and (3) for the four charges and the three chain lengths mentioned, but the results here given are for a chain length of 0.6 D only. The differences which would be produced by the use of longer or shorter chains are, however, referred to when necessary.

(221) From Fig. 42 by taking a chain of length 0.6 D in each of the sixteen positions indicated it is possible to obtain an average value for the total length of chain which is at any instant (a) in the gas, (b) on the lining, or (c) in the material. The result of these measurements, expressed as surface per cent., is shown in Table XXXIII.

TABLE XXXIII.—Distribution of Chain Surface in Kiln.

Charge in kiln per cent.	Per cent. surface of chain.			Remarks.
	In gas.	On lining.	In slurry.	
5	47	13	40	Length of chains 0·6 D.
8	47	9	44	
13	45	7	48	Inclination of surface of charge 15 deg.
20	42	5	53	

(222) DENSITY OF CHAINS IN KILN.—In order to calculate the shielding effect of the chains on the gas radiation to the lining, and to the material chord, the
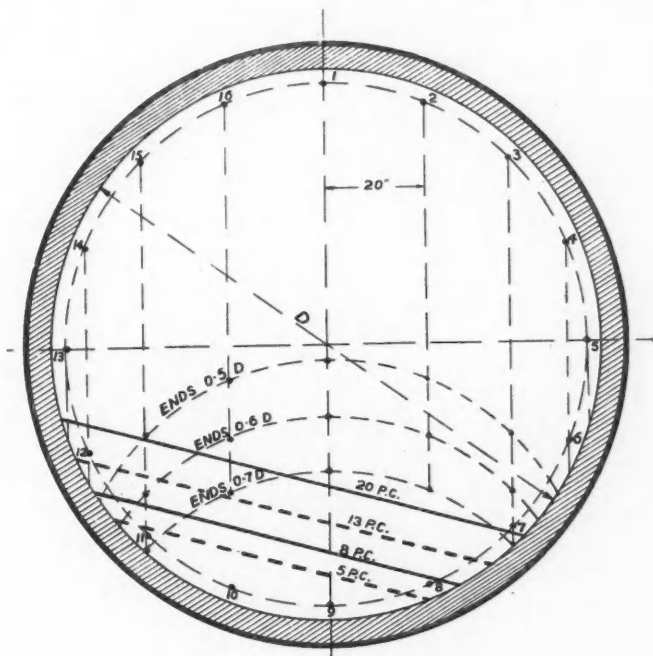

Fig. 42.

surface area of the chain in the gas is conveniently expressed as equal to (in this instance) 45—¾ in. diameter balls per cubic foot of gasway.   Since the links overlap to some extent, seven-eighths of the full surface area is used and the chain surface so reduced is termed the net surface.   The chain density here assumed corresponds to a net surface area of 0.4832 sq. ft. per cubic foot of gasway.

C

Stages (1), (2) and (3), with Chains.—Charge Variable.

(223) The calculations of heat transmission are again made by assuming that each stage forms part of the 400-ft. kiln. The clinker output, see para. (109), is $15\frac{1}{2}$ tons per hour with a standard coal consumption of 24.5 per cent. Further data are given in para. (111) and in Table XIX. A summary of the results obtained is given in Table XXXIV.

The area of the gasway in line (2) is obtained in each stage from lines (5) and (15) of Table XIX. As the charge increases the kiln diameter is increased proportionately [see line (1)], in order to keep the area of the gasway and the gas velocity constant. Under these conditions the kiln output and coal consumption may be assumed to remain unchanged.

(224) To obtain the net chain surface area per foot run of kiln the charge of 8 per cent. in stage (2) is taken as an example. The area of the gasway in cross section is 56.59 sq. ft., hence the net chain surface in the gasway [see para. (222)] is $0.4832 \times 56.59 = 27.34$ sq. ft. From Table XXXIII the net chain surface area in the slurry is $\frac{44}{47} \times 27.34 = 25.60$ sq. ft. and the net chain surface area per foot run of kiln is $\frac{27.34}{0.47} = 58.17$ sq. ft. The calculations proceed generally as in paras. (145) to (150), and the stage length required [see line (7) on Table XXXIV] is found to be 38.2 ft.

The area of the lining surface is evidently $8.85 \times \pi \times 38.2 = 1{,}061$ sq. ft. as shown in line (8), and the area of the chain surface in the stage (net) is $58.17 \times 38.2 = 2{,}220$ sq. ft. as shown in line (9).

For chains of length 0.6 D hung in sixteen rows as shown in Fig. 42, the pitch of the chains will be $10\frac{3}{4}$ in. for an 8 per cent. charge. The chain volume is 1.7 per cent. of the kiln volume, and the volume of the chain buried in the slurry is 9.2 per cent. of the slurry volume. [The chain weight in tons can be found by dividing the figures in line (9) by 254.3 when $\frac{3}{4}$-in. chains are used.]

(225) The figures in lines (8) and (9) show how the rate of heat transmission in each stage is affected at constant output when the charge is varied. · In stage (1) the lining surface required is least at a 5 per cent. charge, and the chain surface required is a minimum for an 8 per cent. charge, but the differences are small. · It is apparent that the charge may be anything between 5 and 13 per cent. without loss of efficiency. In stage (2) the figures indicate that an 8 per cent. charge will give the best result, and the same may be said of stage (3). Hence in stages (1), (2), and (3) there is little or no advantage in using a charge larger than 8 per cent. It may be pointed out, however, that the average chain temperature falls as the charge increases, but this point is not important until the end of stage (3) is reached.

(226) EFFECT OF INCREASING THE CHAIN LENGTH.—Under the conditions shown in Table XXXIV, if the chain length is increased from 0.5 D to 0.7 D with the same chain surface area per cubic foot of gasway it is found for an 8 per cent. charge that (a) the heat transmission per foot run is increased by 1.5 per

cent., (b) the lining surface required is reduced by 1.6 per cent., and (c) the weight of chain required is increased by 6.5 per cent. These figures are average values for stages (1), (2), and (3).

Methods of Suspending Chains.

(227) The method of chain suspension shown in Fig. 42 and on which Table XXXIV is based, differs from that shown in Fig. 23 on which Table XXI is based. In the latter case the chains are suspended at each end, and the distribution of chain surface for an 8 per cent. charge is (approximately) in the gasway 69 per cent., on the lining 4 per cent., and in the material 27 per cent.

Comparing these figures with those shown on Table XXXIII for an 8 per cent. charge it will be seen that when the chains are suspended at one end only a much larger proportion of their surface is buried in the material. This leads to a lower average chain temperature and to a higher rate of heat transmission.

With the method of suspension shown in Fig. 23, the length required for stage (2), with an 8 per cent. charge (see Table XXI) was 46.1 ft. and the weight of chain in the stage was 6.92 tons. The chain surface used per cubic foot of gasway was 0.465 square feet.

TABLE XXXIV.—HEAT TRANSMISSION WITH CHAINS IN STAGES (1), (2) AND (3).
CHARGE VARIABLE. LENGTH OF CHAINS 0.6 D.

			STAGE Nº (1)				STAGE Nº (2)				STAGE Nº (3)			
			Charge per cent.				Charge per cent.				Charge per cent.			
			5	8	13	20	5	8	13	20	5	8	13	20
1	Kiln diameter inside lining	Feet	8·71	8·85	9·10	9·49	8·71	8·85	9·10	9·49	8·49	8·63	8·88	9·26
2	Area of gas way	sq. ft	56·59	56·59	56·59	56·59	56·59	56·59	56·59	56·59	53·84	53·84	53·84	53·84
3	Average gas temperature	deg. fah	587	587	587	587	811	811	811	811	1122	1122	1122	1122
4	Average gas velocity	ft. per sec.	21·8	21·8	21·8	21·8	25·3	25·3	25·3	25·3	29·8	29·8	29·8	29·8
5	Average lining temperature	deg. fah.	173	167	160	155	302	287	272	260	458	421	383	351
6	Average chain temperature	" "	176	172	168	163	302	295	284	273	431	416	393	370
7	Length required for stage	feet	44·9	44·3	43·8	43·1	38·9	38·2	37·3	36·5	26·4	25·6	24·8	23·9
8	Lining surface in stage	sq. ft.	1228	1231	1251	1285	1063	1061	1066	1090	702	692	690	694
9	Chain surface in stage (nett)	" "	2610	2577	2660	2805	2260	2230	2266	2375	1459	1414	1430	1480

When the chains are suspended at one end only, Table XXXIV shows that the length of stage (2) for an 8 per cent. charge is reduced to 38.2 ft., but the weight of chain is increased to 8.73 tons. The chain surface used per cubic foot of gasway was 0.4832 square feet.

Variation of Maximum Chain Temperature with the Charge.

(228) At any cross section of the kiln the temperature of each point of the chain will vary in accordance with the periods during which it is alternately exposed to the hot gases and buried in the material as the kiln revolves. On referring to Fig. 42 it will be seen that a small area at the point of suspension will have the maximum time in the gas and the minimum time in the material. These times will be affected by the volume of the charge but not by the length of the chain.

(229) The chain temperatures at the point of suspension for various charges have been worked out for a cross section at the end of stage (3). In this position the slurry is half dry, and chains are not usually taken much farther down the kiln.

The gas temperature at the end of stage (3), see Table XVIII, is 1,296 deg. F., and the average lining temperature when chains are used is 542 deg. F. The times during which a small area at the chain suspension is in the gas and in the material for each charge can be obtained from Fig. 42 and the average chain temperature is then found by trial.

(230) A typical calculation is based on 1 sq. ft. of chain surface (net) with an 8 per cent. charge, and the average chain temperature is assumed to be 766 deg. F. The time in the gas is found to be 0.783 minute, and the heat received in that period is 110.3 B.T.U. The chain radiates 20.3 B.T.U. to the adjacent lining surface, leaving a gain of 90 B.T.U.

The square foot of chain surface is buried in the material (which is at a temperature of 212 deg. F.) for 0.217 minute and during this period, with a value of $H_{con} = 45$ and a temperature difference of 554 deg. F., the heat given up is also 90 B.T.U. Hence the average chain temperature assumed is correct.

The weight of chain, which has a net surface of 1 sq. ft., is 8.8 lb. and the specific heat of iron is 0.115, hence the fluctuation of the chain temperature will be

$$\frac{90}{8.8 \times 0.115} = 89 \text{ deg. F.}$$

(231) The P.D. values for gas radiation and the convection constants are averaged from Table XIX. Also the shielding co-efficients for the radiation between the gas and the chains and between the chains and the lining have been estimated and allowed for. The calculation results for four charges are shown on Table XXXV.

TABLE XXXV.—MAXIMUM CHAIN TEMPERATURES AT THE END OF STAGE (3).

Charge in kiln per cent.	Time in gas, minutes.	Time in material, minutes.	Chain temperature range per revolution deg. Fah.
5	0·825	0·175	774 to 852
8	0·783	0·217	721 to 811
13	0·731	0·269	661 to 759
20	0·675	0·325	598 to 702

It will be seen that as the charge in the kiln increases the chain temperature falls.

Summary.

(232) The general tendency of paras. (223) to (226) is to show that in stages (1), (2) and (3), which occupy nearly half the length of the kiln, there is little or no advantage in exceeding a charge of 8 per cent. or a chain length of 0.6 D. At the extreme end of stage (3), however, a large charge may be useful since it tends to keep down the temperature of the chain.

The Drying Zone of the E.L.Z. Kiln.

(233) A kiln having zones extra large in diameter for drying the slurry and for decomposing the $CaCO_3$ was described in Part IX, and the general effect of the enlarged decomposition zone was made clear. It is now proposed to deal

with the enlarged drying zone marked B on Fig. 34.   The diameter inside the lining is 14.6 ft., and it would mainly be occupied by stages (1) and (2).   It is not proposed to compare the rate of drying claimed by the makers with that obtained in kilns of more usual design, since in the E.L.Z. kiln the slurry is sprayed against the chains in accordance with a patented system and this inquiry is restricted to the effect of changes in the kiln diameter and in the charge per cent.

With this limitation in mind, it may be said that an enlarged drying zone is not advantageous.   It enables, for instance, a 20 per cent. charge to be carried, but Table XXXIV shows generally that an 8 per cent. charge gives a somewhat better rate of heat transmission.   The main drawback to an enlarged drying zone is that the gas velocity through it becomes relatively small and the rate of heat transfer to the chains by convection falls off.   The enlarged diameter gives greater P.D. values for gas radiation, but when the stage diameter exceeds 8 to 10 ft. the corresponding increase in the rate of heat transmission in stages (1) and (2) is small.

(234) Using stage (2) for purposes of comparison, the leading details of the heat transmission for a kiln based on the 400-ft. kiln and for the E.L.Z. kiln are shown on Table XXXVI.

TABLE XXXVI.—Comparison in Stage (2) of Kilns with and without Enlarged Zones.

Line No.			Normal kiln.	E.L.Z. kiln.
(1)	Kiln diameter inside lining .. .. ft.		8·85	14·60
(2)	Charge in kiln .. .. per cent.		8·0	20·0
(3)	Clinker output .. ..tons per hour		15·50	13·33
(4)	Chain surface in gas, per cubic foot of gasway (net).. sq. ft.		0·4832	0·4832
(5)	Gas velocity .. .. ft. per second		25·3	9·3
(6)	Convection } Gas and lining or material		2·15	0·97
(7)	Constants H_e } Gas and chains		11·0	6·9
(8)	Length required for stage (2) .. .. ft.		38·2	20·4
(9)	Per clinker } Lining surface required .. .. sq. ft.		68·5	70·0
(10)	ton per hour } Weight of chains required .. .. lb.		1,260	2,075

Lines (1) to (3).—The details of the normal kiln are taken from para. (111) and from Table XXXIV for a charge of 8 per cent. in stage (2).   The diameter and the clinker output of the E.L.Z. kiln are taken from para. (192), but the working conditions as regards percentage coal consumption and the gas composition and temperature are again assumed to be similar to those of the 400-ft. kiln.

Line (4).—The net chain surface in the gas, per cubic foot of gasway, see para. (222), is made the same for each kiln ; actually the chain surface in the E.L.Z. kiln was somewhat less.

Line (5).—The relatively low gas velocity in the case of the E.L.Z. kiln is due to the larger diameter and to the smaller output.

Lines (6) and (7).—The effect of the lower gas velocity is seen in the smaller values of H_e.

Lines (9) and (10).—It will be seen, finally, that the E.L.Z. kiln requires for each ton of clinker per hour (*a*) slightly more lining surface and (*b*) considerably more chain. These figures are for stage (2).

Summary of Parts IX and X.

(235) The inquiry into the effect of wide changes in the kiln diameter and in the charge per cent., as recorded in Parts IX and X, shows generally that a kiln (with or without chains) will have the highest rate of heat transmission when both the diameter and the charge per cent. are relatively large at the hot end of the kiln and small at the cold end. For chains suspended at one end a suitable length is 0.6 *D*. It would not be necessary to build a decomposition zone extra large in diameter if a uniform charge of 12 to 15 per cent. throughout the zone could be otherwise obtained.

Correction to Part IX.—The power required to turn the decomposition zone, see paras. (203), (204) and (206), depends on the horizontal distance of the centre of gravity of the charge from the vertical centre line of the kiln, hence the figures given should be multiplied by $\sin \phi$, where ϕ is the slope of the surface of the charge. Taking ϕ at 40 deg., the horse-powers required are : normal kiln 8.8, E.L.Z. kiln 41.2.

Abstracts from the Foreign Press.

Effect of Salts on Portland Cement. By R. Grün and H. Marecke (*Tonindustrie-Zeitung*, Nos. 21 and 22, 1934).—Solutions of the chlorides of metals of equal molecular concentration shorten the setting time in the order Mg, Ca, Fe, Al. Mixtures of salts have, in general, effects lying between those of the salts themselves, except for the mixture $CaCl_2$—$FeCl_3$ which is more effective in shortening the setting time than either salt alone. The compressive strength of $3 : 1$ mortar is lowered by molecular concentrations of 1·0 and over in the gauging water for $CaCl_2$ and $AlCl_3$, but improved by molecular concentrations under 0·5. $CaCl_2$ raises the strength at twelve and twenty-four hours, whereas the advantage of $AlCl_3$ is noted only after three days. $MgSO_4$ and $Al_2(SO_4)_3$ adversely affect strength ; the latter in molecular concentrations of 1·0 produces unsoundness.

High-strength Cements. By F. Ferrari (*Tonindustrie-Zeitung*, No. 53, 1934). A cement with very good qualities has been prepared with hydraulic modulus 2·2 to 2·3, silica ratio 3·0 to 3·3, and alumina to iron ratio 1·6 to 0·6. The slurry is easy to burn. Concrete made with this cement has exceptional workability, a low evolution of heat, very small shrinkage, and high resistance to sulphate waters. It is highly suitable for mixing with pozzolana and blastfurnace slag. The iron content is raised by adding spent pyrites to the raw material. The production of this cement was patented in Europe and the U.S.A. in 1919 and 1920.

Compound Flame Furnace for the Burning of Cement.

By N. C. KYRIACOU.

THE flame furnace enables the maximum amount of heat to be produced in the minimum time and at the highest temperatures obtainable in practice. If, in addition, the installation of powerful plant capable of high production rates is included, the importance of the flame furnace is seen. For instance, smelting furnaces recently installed in Rhodesia are of the flame furnace type, 7.62 metres wide by 30.5 metres long ; they are equipped with four burners, and the fuel consumption exceeds 100 tons of coal dust per day. Nevertheless, the flame furnace of present-day design is inefficient, chiefly due to the high temperature of the gases which as they leave the furnace carry with them 30 per cent. of the heat produced. Several remedies have been proposed, the addition to the flame furnace of heat-recovery boilers being the system most generally employed.

The flame furnace, owing to the hung construction of its main arch, may be increased in size now that adequate refraction is possible by the use of a material such as radex, sillimanite, or bricks of cast bauxite, simensite, etc. The reduction in heat production, and particularly the degree of temperature obtained, leaving out of consideration ideal conditions of combustion without excess fuel consumption, are entirely dependent on pre-heating the air for combustion purposes and developing the flame as fully as possible. Thus if air at 0 deg. C. is used the temperature of combustion is merely 1,600 deg. C., whereas if the air is pre-heated to 200, 400 or 600 deg. C., this temperature may reach 1,735, 1,875 or 2,015 deg. C. respectively. The importance of the drop in heat production is well illustrated in the example given by Rosin. To melt chromium and sulphur requires the same amount of heat, approximately 200 calories per kilogramme, but it is only possible to obtain the same effect with the two materials if allowance be made for a difference of 70 per cent., due to the fact that the melting point of chromium is one of the highest known, whereas the low melting point of sulphur enables the entire heat potential to be used.

The transmission of heat by the flame furnace takes place by radiation and convection. The first process is by far the more important. Radiant heat is directed by the flame directly on to the material to be treated and also into the gas-filled atmosphere and on to the refractory walls of the furnace which throw back the heat received.

Heat transmission by radiation increases with the difference of the fourth power of the absolute temperature. A rise in temperature of the medium results in considerable heat radiation. Thus at 200 deg. C. the heat radiation from a black substance may be estimated at 2.4×10^3 calories per square metre per hour ; at 1,000 deg. C. this figure rises to 125×10^3 calories per square metre per hour, while at 2,000 deg. C. a radiation of 490×10^3 calories per square metre per hour is attained.

Heat transmission by convection is governed by entirely different laws.   In this case it is necessary for the gases to be kept in close contact with the material to be treated, and the gases must have a very high kinetic velocity.   For instance, if we consider the first three-fourths of the length of an ordinary cement rotary kiln 100 metres long and which functions under the influence of heat transmitted by convection, the slurry may travel as far as half way along the kiln before any alteration in its composition may be detected.   The thick paste acts like a solid impervious body which the gases cannot penetrate.   This demonstrates the inefficiency of the ordinary rotary kiln considered as an apparatus working by heat convection, and is the cause of its low efficiency and of the high temperature of the exit gases.   Conditions are much the same in a metallurgical flame furnace, and explain the high temperature of the waste gases which carry away 30 per cent. of the heat produced.

A number of improvements have been suggested with a view to improving these conditions, such as furnaces with heat-recovery boilers, air heaters, etc., but none of these devices can be deemed an ideal solution or one that really increases the efficiency of the furnace.
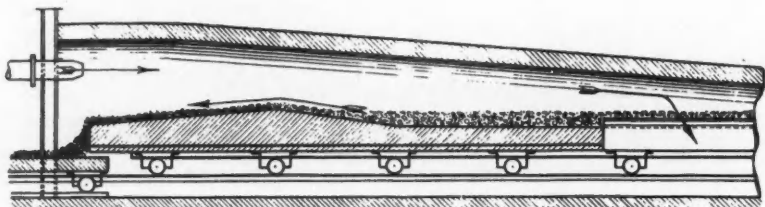
Fig. 1.—Compound Flame Furnace.

Another recent suggestion is suction heating, whereby the gases are drawn through the material and penetrate throughout the mass.   By this system, which has been adopted in metallurgy, the gases lose the greater part of their heat content.   The underlying principle of the device is as follows : If in a vertical kiln a column 10 metres high is required to lower the temperature of the combustion gases to about 150 deg. C., the same results can be obtained with a height of 25 cm. if the material to be treated is lying on a grate and if the gases pass from the upper side to the lower side, penetrating it thoroughly.   With the aid of this theoretical and practical data, the author has built a compound flame furnace, of which the main characteristic is that the sole or a part of it is formed by a grate through which the combustion gases may be drawn from top to bottom. Patents have been obtained for this apparatus in all industrial countries.

Thus the heat process is divided into two theoretically ideal parts ; melting or clinkering in the combustion zone is by radiation, and pre-heating or calcination on the grate is by convection.   As the combustion gases are drawn through the grate the entry of excess air into the apparatus is impossible and the exterior radiating surface is reduced to a minimum.

The passage along the grate of the material to be treated is carried out by oscillatory, vibratory, or similar movement of the grate. The compound flame furnace consists of a fixed suspended arch made of first-class refractory material resisting the highest possible temperatures. The sole and/or the grate, which is not submitted to the high temperatures of the medium since it is covered by the material to be treated, may be made of cinder concrete or, in the case of the grate, of steel sections.

With the smelting flame furnace is merely combined a grill on to which the material to be treated is fed as required. The combustion gases reach this part of the furnace at a temperature of 900 to 1,000 deg. C., and pass through the material to be treated from top to bottom. In the course of their passage through the material the gases lose the greater portion of their heat and cool down to about 120 deg. C., when they are then sucked off by a fan and pass into the atmosphere.

The clinkering flame furnace, as designed for cement manufacture in combination with a grate, consists of a fixed suspended arch, which may reach considerable dimensions, made of first-class refractory material enabling extremely high temperatures to be obtained and thus improving the efficiency of the
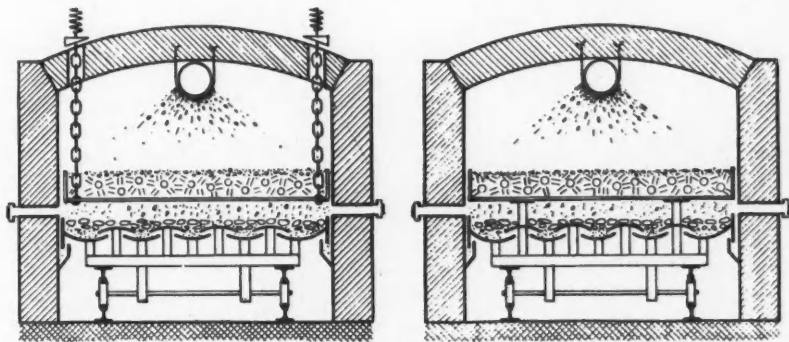
Fig. 2.—Vibratory Grate for use in Wet Process.

apparatus. The sole and grate, which may be made in one piece, are not exposed to the high temperatures of the surrounding medium as they are covered by the material to be treated. Part of the sole is solid and made of cinder concrete or other refractory material, whereas the remainder, forming the grate, may be built of sectional steel. An important detail is that the gas openings or slots are parallel to the furnace. Both sole and grate, whether combined or separate, are mounted on rollers and given an irregular oscillating movement by means of an elliptical reducing gear so as to cause the material to travel forward.

The output of the furnace is very high, owing to the possibility of obtaining a sole of maximum width and one which corresponds to the clinkering zone of the largest modern flame furnace. It is also necessary to take into account

the fact that in the rotary kiln, for instance, the working width or arc, of the zone heated by radiation, does not exceed one-seventh of its circumference, whereas in the flame furnace the width of the sole corresponds to that of the clinkering zone.

For a cement furnace of this description, to transmit the oscillating movement to a 1 m. by 18 m. sole, a 20 h.p. motor is all that is required.   The elliptical speed-reduction gear providing the oscillating movement is directly driven by a direct-current motor and the rate of travel of the material is easily controllable ; for instance, with a 300-mm. stroke at a speed of 42 revolutions per minute, the crushed material is turned over without moving forward, while if the speed is increased the material travels forward.   The rate of travel can be accurately regulated without stopping the motor.   As for the strength of the shaking mechanism, it may be mentioned that most coal mine conveyors are of the oscillating type, and potassium mines use conveyors of the same type with an output of 300 tons and a length of 120 metres.   A flame furnace combined with a supplementary grate charged with bodies capable of storing heat, such as hollow cylinders or solid balls, and fed with slurry, may by continuous or intermittent pulverisation be used for the preparation of cement by the wet process.

The slurry will be pulverised intermittently by the heat-retaining bodies on the drying grate.   The hot gases drawn across these bodies bring them to a high temperature, and owing to their high heat capacity, which is about 2,000 times higher than that of the combustion gases, the drying process commences immediately. The vibratory movement of the grate dries and granulates the slurry, which subsequently falls on to the main calcining grate, from which point it follows the usual process.

This arrangement may also be used in the usual type of rotary kiln for drying the raw cement slurry efficiently.   It would appear that the compound flame furnace may be used with advantage for any heat treatment, such as the desiccation, calcination, distillation, pre-heating and clinkering of various products.

Air Elutriation of Cement with Electrical Separation.   By T. KITAZAWA. (*Rev. Assoc. Jap. Port. Cem. Engrs. Osaka*, 1932, pp. 23–24.)—It was found that the well-known air elutriator gave inaccurate results due to the particles blocking the pores of the flannel bag filter and reducing the flow of air.   To overcome this difficulty electrical deposition of the dust was used.   A positive pole consisting of a wire 100 cm. long was suspended in the elutriator tube to two-thirds of its length ; the tube formed the negative pole.   When a difference of potential of 20,000 volts was maintained between the two electrodes the fine cement particles were removed from the air stream and deposited on the tube wall.   The working of the process depends on the tube diameter, the speed of the air stream, the voltage, the length of the positive pole, and the particle size of the cement. Tests showed that 95 to 97 per cent. of the dust was deposited on the wall under the following conditions : Tube diameter, 7 cm. ;   length of positive pole, 100 cm. ;   voltage, 15,000 ;   particle size of cement, < 20 microns.

Components and Systems Having a Possible Bearing on Portland Cement Clinker Constitution.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

(Concluded.)

Formation of Calcium Silicates in the Presence of Water

The work of Baylis[32] on the adsorption of calcium hydroxide by silica gel and on the extraction of the adsorption product with water appears to show that a definite compound is formed on adsorption, containing calcium oxide and silica in equimolecular proportions. This compound is able to take up still further calcium hydroxide and there exists a reversible equilibrium between the adsorbed lime and the solution in contact with it.

Jolibois and Chassevent[33] investigated the reactions between solutions of lime and colloidal silica. Solutions containing 0.063 gr. calcium oxide per litre showed the formation of a hydrated monocalcium silicate.

THE SYSTEM CALCIUM OXIDE-SILICA.[34][35]—Calcium oxide and silica when heated together can unite to form four distinct compounds : (1) the metasilicate, $CaO.SiO_2$; (2) the compound, $3CaO.2SiO_2$; (3) the orthosilicate, $2CaO.SiO_3$; (4) tricalcium silicate, $3CaO.SiO_2$. Some of these compounds occur in more than one crystalline modification.

(1) CALCIUM METASILICATE, $CaO.SiO_2$ ($CaO = 48.2\%$, $SiO_2 = 51.8\%$).— This occurs in two modifications, namely, a-$CaO.SiO_2$ (pseudo-wollastonite) and β-$CaO.SiO_2$ (wollastonite). At 1,200 deg. C. there is a reversible inversion

TABLE III.—OPTICAL PROPERTIES.

	a-$CaO.SiO_2$.	β-$CaO.SiO_2$.
Crystal system	Probably monoclinic (pseudo-hexagonal).	Monoclinic.
Crystal habit	Irregular interwoven grains showing no decisive crystalline outline.	Plates. Laths. Cleavage parallel to the elongation of the laths and fibres is well marked.
Refractive index .... (sodium light.)	a 1.610 β 1.611 γ 1.654	a 1.616 β 1.629 γ 1.631
Birefringence	Strong ; $\gamma - a =$ about 0.042	Medium ; $\gamma - a =$ about 0.015.
Optic axial angle	Very small.	$2E = 70$ deg.
Optical character	Positive.	Negative.
Remarks	Polysynthetic twinning is not uncommon.	Resembles the natural mineral in every respect.

point, a-$CaO.SiO_2$ being stable above this temperature and β-$CaO.SiO_2$ below it. a-$CaO.SiO_2$ has never been observed in nature, but only in artificial melts and slags ; the melting point is 1,540 deg. C. It can take up about 2 per cent. of

either lime or silica in solid solution ; these additions affect the inversion point, the lime lowering it to 1,190 deg. C., while the silica raises it to 1,210 deg. C.

β-CaO.SiO$_2$ can be obtained artificially by heating a mix of the correct composition to a temperature not exceeding 1,200 deg. C.

(2) THE COMPOUND 3CaO.2SiO$_2$(CaO = 58.2%, SiO$_2$ = 41.8%).—This body dissociates into α-dicalcium silicate and liquid at 1,475 $\pm$ 5 deg. C. and consequently shows no true melting point. It is best prepared by holding glass of the composition 3CaO.2SiO$_2$ at a temperature slightly below 1,475 deg. C. until crystallisation occurs. Its optical properties are : crystal system, probably orthorhombic ; crystal habit, rounded irregular grains without definite crystal outline and without distinct cleavage ; refractive index (sodium light), α = 1.641, γ = 1.650 ; birefringence, fairly weak ($\gamma - \alpha$ = about 0.01) ; optic axial angle, large ; optical character, positive.

(3) CALCIUM ORTHOSILICATE, 2CaO.SiO$_2$(CaO = 65%, SiO$_2$ = 35%).—There are three major modifications of this compound. γ-2CaO.SiO$_2$ is only stable below 675 $\pm$ 5 deg. C., for at this temperature it changes to β-2CaO.SiO$_2$; at 1,420 deg. C. β-2CaO.SiO$_2$ passes into α-2CaO.SiO$_2$ which melts at 2,130 $\pm$ 20 deg. C. without decomposition. The β to γ inversion at 675 deg. C. is accompanied by a 10 per cent. increase in volume which causes the material to disintegrate to a fine powder ; this phenomenon is commonly known as dusting. The inversion may be prevented by the addition of 1 per cent. B$_2$O$_3$ or Cr$_2$O$_3$.

Hansen and Bogue[55] have pointed out that in the CaO-Al$_2$O$_3$-SiO$_2$ system this inversion can be prevented by small amounts of alumina. On the other hand the inversion is inhibited only by a high concentration (45 per cent.) of ferric oxide. This supports the theory that it is the glass present in Portland cement clinker which prevents the conversion into the γ-2CaO.SiO$_2$, since no glass is observed in the CaO-Fe$_2$O$_3$-SiO$_2$ system. Probably, therefore, only a small amount of the ferric oxide of Portland cement clinker can be present as the crystalline compounds 2CaO.Fe$_2$O$_3$ and CaO.Fe$_2$O$_3$.

γ-2CaO.SiO$_2$ is easily prepared. The reaction
$$2CaCO_3 + SiO_2 = 2CaO.SiO_2 + 2CO_2$$
is very rapid above 1,200 deg. C., and the inversions of α to β to γ are rapid and complete on cooling. The correctly proportioned mixture is heated twice in a platinum vessel in an electric furnace at 1,450 deg. C. It dusts completely on cooling. β-2CaO.SiO$_2$ is prepared by adding 1 per cent. of Cr$_2$O$_3$ or B$_2$O$_3$ to a mixture of the composition 2CaCO$_3$ + SiO$_2$ and heating in a platinum vessel in an electric resistance furnace for one hour at 1,550 deg. C.
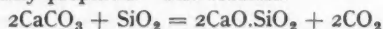
β'-2CaO.SiO$_2$ is an unstable or monotropic compound and is formed occasionally in charges rapidly cooled from a temperature of about 1,400 deg. C.

Of the forms of dicalcium silicate, the high temperature modifications α and β are most common in Portland cement clinker. Bates[39] found that in well-burned commercial clinkers dicalcium silicate occurs largely as the β form. The γ form is not found to any extent except in underburned clinkers which dust on cooling.

The optical properties of the dicalcium silicates[34][36] are—Crystal system : a monoclinic or triclinic, β orthorhombic or monoclinic, γ probably monoclinic. Crystal habit : a irregular grains intricately interwoven, β irregular rounded grains often prismatic in shape, β' grains, γ prismatic.   Refractive index (sodium light) : a dicalcium silicate, $a = 1.715$, $\beta = 1.720$, $\gamma = 1.737$; β dicalcium silicate, $a = 1.717$, $\gamma = 1.735$; β' dicalcium silicate, $\gamma = 1.715$; γ dicalcium silicate, $a = 1.642$, $\beta = 1.645$, $\gamma = 1.654$.   Birefringence : a rather strong, $\gamma - a = 0.022$ (about) ; β medium, $\gamma - a = 0.017$; β' very weak ; γ $\gamma - a = 0.012$.   Optic axial angle : a large, β large, β' very small or uniaxial, γ $2E = 52$ deg.   Optical character : a positive, β positive, β' positive, γ negative.

The optical properties of the a and β forms are, unfortunately, so similar that it is often exceedingly difficult to distinguish between them.   According to Rankin and Wright[34] intricate polysynthetic twinning is characteristic of the a modification.   Hansen,[4] however, considered that the β form can exhibit twinning.   The tendency of this form to twin is accentuated by the strains set up by the a to β inversion so that twinning is characteristic of the samples made by inversion from the a form, while the β form, not showing twinning, is only seen in grains produced by heating below 1,420 deg. C.   The birefringence of the β form appears also to be slightly weaker than that of the a form. γ-dicalcium silicate is readily distinguished from the other forms of dicalcium silicate by its lower refractive index and its optical character.

TRICALCIUM SILICATE, $3CaO.SiO_2$ ($\%CaO = 73.59$, $\%SiO_2 = 26.41$).—This is the most basic calcium silicate.   It is difficult to prepare in a pure state because it dissociates without melting at 1,900 deg. C. $\pm$ 20 deg. C. into a-dicalcium silicate and calcium oxide.   All early attempts to synthesise this compound failed.   On heating together calcium carbonate and silica in the proper ratio only a mixture of dicalcium silicate and calcium oxide was produced. All fusion methods were unsuccessful and yielded the same products. Le Chatelier[58] claimed to have prepared it by decomposing calcium chlorosilicate with water vapour at above 450 deg. C. according to the reaction

$$2CaO.SiO_2.CaCl_2 + H_2O = 3CaO.SiO_2 + 2HCl \uparrow$$
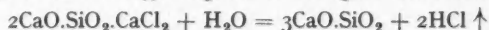
The reaction was incomplete, however, and the product could not be studied microscopically since it appeared amorphous.   It seemed to possess setting and hardening properties ;   pats showed no swelling or cracking, indicating absence of free CaO.   The absence of free CaO together with hydraulic properties not possessed by the lower silicates indicated that the compound was tricalcium silicate.

The Newberrys[59] claimed to obtain a sound hydraulic product by heating an intimately ground mixture of $3CaCO_3 + SiO_2$ at white heat.   Richardson[60] heated a finely ground homogeneous mix of $3CaO + SiO_2$ for three hours at 1,650 to 1,700 deg. C. and obtained a snow-white, sintered, porous, and non-dusting product, although it crushed readily in the fingers.   He considered that some tricalcium aluminate was present due to impurities in the raw mix.

According to Campbell[61] large crystals of tricalcium silicate can be obtained by very slowly cooling a solution of dicalcium silicate and calcium oxide in $5CaO.3Al_2O_3$ as solvent. Nagai and Asaoka[37] reported that tricalcium silicate is only formed with great difficulty in the absence of aluminates and ferrites. The reaction $2CaO.SiO_2 + CaO \longrightarrow 3CaO.SiO_2$ is extremely slow at temperatures up to 1,600 deg. C. Rankin[34] observed that calcium oxide became less reactive when it was heated at high temperatures.

The following two methods of preparation have been successfully used by American workers.[4]

Method A.—(1) A finely ground mixture of the molecular composition $2.3CaCO_3 + SiO_2$ is heated in a platinum vessel in an electric furnace for one hour at 1,550 deg. C. (2) The product from (1) is reground with 0.3 mol. wt. $CaCO_3$ and reheated. (3) The product from (2) is reground with 0.3 mol. wt. $CaCO_3$ and reheated. (4) The product from (3) is reground with 0.1 mol. wt. $CaCO_3$ and reheated. (5) The product from (4) is reground and reheated.

Method B.—(1) A mixture of $4CaCO_3 + SiO_2$ is heated for one hour at 1,500 deg. C. (2) The product from (1) is ground to a stiff paste with distilled water and reheated at once. By this process no appreciable disintegration of tricalcium silicate occurs, but free calcium oxide is hydrated to calcium hydroxide and this yields reactive calcium oxide at higher temperatures. (3) The product from (2) is found optically to be largely tricalcium silicate and calcium oxide. Some crystals of γ-$2CaO.SiO_2$ are present. The product is reground with water and reheated. (4) The product from (3) still contains some grains of γ-$2CaO.SiO_2$; it is reground with water and reheated. (5) The product from (4) is heated with hot absolute alcohol and glycerine whereby free calcium oxide is dissolved and is then neutralised with alcoholic ammonium acetate. The suspension is filtered and the residue washed once with absolute alcohol. It is then reheated. (6) The product from (5) contains a little free calcium oxide. This is removed as in (5) and the product reheated. (7) A small charge of the product from (6) is heated for 48 hours at 1,500 deg. C.

The optical properties of tricalcium silicate are—Crystal system : probably monoclinic. Crystal habit : minute colourless grains showing no definite crystal outline ; twinning lamellæ not uncommon. Refractive index (sodium light) : $\gamma = 1.715 \pm 0.002$. Birefringence : very weak (not more than 0.005). Optic axial angle : very small or uniaxial. Optical character : negative.

Dicalcium silicate retains the apparent structure of the γ modification for some time at temperatures considerably above the γ to β inversion temperature, although the refractive index is now that of β-dicalcium silicate. In this way tricalcium silicate formed by the combination of this dicalcium silicate with calcium oxide at 1,500 deg. C. may contain some crystals similar in appearance to γ-dicalcium silicate. Their mean refractive index and birefraction are, however, those of tricalcium silicate.

THE SYSTEM CALCIUM OXIDE-ALUMINA[28 34 38 39 40]—There are according to Rankin and Wright[28 34] only four compounds of calcium oxide and alumina, namely, (1) $3CaO.Al_2O_3$, tricalcium aluminate ; (2) $5CaO.3Al_2O_3$, exists in two

forms ;   (3) $CaO.Al_2O_3$, monocalcium aluminate ;   (4) $3CaO.5Al_2O_3$, exists in two forms.

Stern[41] heated various mixtures of calcium carbonate, silica, and alumina up to 1,600 deg. C. and cooled them slowly.   He concluded that there was evidence of crystallisation of dicalcium aluminate, $2CaO.Al_2O_3$, from a eutectic.   Several workers from time to time have concluded that such a body exists, but Koyanagi[42] in 1931 pointed out that it is a mixture of $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$.   He, however, claimed to have obtained a new aluminate with the formula $3CaO.2Al_2O_3$. He described this as crystallising in well-developed spheroliths which showed blue and yellow interference colours in thin section under crossed nicols.   This body sintered at 1,250 deg. C. approximately and melted at 1,300 deg. C. Koyanagi stated that these spheroliths were not the same as those of the labile form of $5CaO.3Al_2O_3$.

TRICALCIUM ALUMINATE, $3CaO.Al_2O_3$ (%CaO = 62.22, %Al_2O_3 = 37.78).—This body dissociates at 1,535 deg. C. into calcium oxide and liquid.   It is prepared by heating a finely ground mixture of pure precipitated calcium carbonate and alumina in the correct proportions in an electric furnace at 1,375 ± 10 deg. C. for some time.   The product is ground up and reheated to the same temperature and finally the process is repeated.   A temperature of 1,375 deg. C. is chosen because $5CaO.3Al_2O_3$ and $3CaO.Al_2O_3$ form a eutectic with a melting point of 1,395 deg. C. and formation of liquid makes the product more difficult to grind.

Campbell[43] considered that a binary system of calcium oxide and alumina containing more than 47.8 per cent. CaO (which is equivalent to $5CaO.3Al_2O_3$) should be regarded as a study in solubility of calcium oxide in $5CaO.3Al_2O_3$. Tricalcium aluminate should be regarded either as a metastable solid solution of calcium oxide in $5CaO.3Al_2O_3$ or as $5CaO.3Al_2O_3$ with 4 molecules of calcium oxide of crystallisation rather than as a stable phase in the strict sense of the word.   On the other hand Rankin and Wright[28] [34] reported that tricalcium aluminate is a stable phase in all binary mixtures containing more than 47.8 per cent. CaO and at all temperatures up to 1,535 deg. C.

$5CaO.3Al_2O_3$ (%CaO = 47.78,   %Al_2O_3 = 52.22).—This body melts at 1,455 deg. C. without decomposition.   It may be prepared by fusion of the correct mix in an electric furnace, but its formation commences much below the melting point.[44]   It exists in two forms, namely, a stable form and an unstable monotropic modification.   The unstable variety has neither a definite melting point nor any temperature range of real stability.   It is obtained under special conditions of cooling and is usually not well developed in single crystallites.

MONOCALCIUM ALUMINATE, $CaO.Al_2O_3$ (%CaO = 35.44, %Al_2O_3 = 64.56).—This body melts at 1,595 deg. C. without decomposition.   It may be prepared by heating the correct mix to fusion or heating at lower temperatures for a longer time.   Nagai and Naito[44] pointed out that heating of the correct mix at as low a temperature as 1,250 deg. C. for seven hours yields 90 per cent. $CaO.Al_2O_3$.

$3CaO.5Al_2O_3$ (%CaO = 24.78, %Al_2O_3 = 75.22).—This compound crystallises in two forms : (1) stable, and (2) unstable, and apparently monotropic with

respect to (1). (1) melts at 1,720 deg. C. It is prepared by heating the correct mix to a temperature exceeding 1,600 deg. C. for some time, cooling, grinding, and reheating. Monocalcium aluminate is first formed and combines with alumina as the temperature is raised. (2) crystallises occasionally from the rapidly cooled liquid. It has no definite melting point and apparently no definite region of real stability ; it inverts so rapidly at high temperatures to the stable form that perfectly homogeneous preparations cannot be obtained.

The optical properties of the calcium aluminates are—Crystal system : $3CaO.Al_2O_3$, isometric ; stable $5CaO.3Al_2O_3$, isometric ; unstable $5CaO.3Al_2O_3$, probably orthorhombic ; $CaO.Al_2O_3$, probably monoclinic ; stable $3CaO.5Al_2O_3$, tetragonal ; unstable $3CaO.5Al_2O_3$, probably orthorhombic. Crystal habit : $3CaO.Al_2O_3$, colourless grains often hexagonal or rectangular in outline ; stable $5CaO.3Al_2O_3$, irregular rounded grains ; unstable $5CaO.3Al_2O_3$, fibrous and prismatic ; $CaO.Al_2O_3$, irregular crystals tending towards prismatic development ; stable $3CaO.5Al_2O_3$, colourless grains often with indications of rectangular outline ; unstable $3CaO.5Al_2O_3$, prismatic to fibrous with fair prismatic cleavage. Refractive index (sodium light) : $3CaO.Al_2O_3$, $\gamma = 1.710$; stable $5CaO.3Al_2O_3$, $\gamma = 1.608$; unstable $5CaO.3Al_2O_3$, $a = 1.687$, $\gamma = 1.692$; $CaO.Al_2O_3$, $a = 1.643$, $\beta = 1.655$, $\gamma = 1.663$; stable $3CaO.5Al_2O_3$, $a = 1.617$, $\gamma = 1.652$; unstable $3CaO.5Al_2O_3$, $a = 1.662$, $\beta = 1.671$, $\gamma = 1.674$. Birefringence : unstable $5CaO.3Al_2O_3$, weak ; $CaO.Al_2O_3$, rather strong $(\gamma - a = $ about $0.02)$; stable $3CaO.5Al_2O_3$, strong $(\gamma - a = $ about $0.035)$; unstable $3CaO.5Al_2O_3$, medium $(\gamma - a = 0.013)$. Optic axial angle : unstable $5CaO.3Al_2O_3$, apparently large ; $CaO.Al_2O_3$, $2V = 36° \pm 4°$; stable $3CaO.5Al_2O_3$, uniaxial (indications of biaxial character, with small $2E$ noted occasionally) ; unstable $3CaO.5Al_2O_3$, $2V = 35° \pm 5°$. Optical character : unstable $5CaO.3Al_2O_3$, apparently negative but difficult to determine because of overlapping fibres ; $CaO.Al_2O_3$, negative ; stable $3CaO.5Al_2O_3$, positive ; unstable $3CaO.5Al_2O_3$, negative. Remarks : $3CaO.Al_2O_3$, occasionally grey interference colours appear as a result of strain ; unstable $5CaO.3Al_2O_3$, occurs as radial spherulites or aggregates of overlapping, and often approximately parallel, fibres ; colour usually pale green ; the more deeply coloured grains are pleochroic, $a = $ blue green, $\gamma = $ olive green ; absorption, $a < \gamma$; $CaO.Al_2O_3$, complex twinning is a characteristic feature ; unstable $3CaO.5Al_2O_3$, axial dispersion strong.

THE SYSTEM CALCIUM OXIDE-FERRIC OXIDE.—Michaelis[62] considered that $3CaO.Fe_2O_3$ did not exist, the product being unsound. This opinion was supported by Newberry and later by Campbell.[64] Sosman and Merwin[45] studied the $CaO-Fe_2O_3$ system by temperature-time curves controlled by optical examination of the products. Only two compounds could be formed, namely, mono and dicalcium ferrites, $CaO.Fe_2O_3$ and $2CaO.Fe_2O_3$. Neither CaO nor Fe_2O_3 formed solid solutions with either $CaO.Fe_2O_3$ or $2CaO.Fe_2O_3$, but CaO dissolved to some extent in Fe_2O_3. No evidence was obtained of the existence of $3CaO.Fe_2O_3$ or of $5CaO.3Fe_2O_3$, the latter compound having been suggested by Campbell.[64] Instead of being analogous to the system $CaO-Al_2O_3$ the diagram of the system $CaO-Fe_2O_3$ resembles that of $MgO-SiO_2$. Campbell,[64] following

the work of Sosman and Merwin, admitted that the body $5CaO.3Fe_2O_3$ suggested by him was really a mixture of $2(2CaO.Fe_2O_3) + CaO.Fe_2O_3$.

According to Hilpert and Kohlmeyer[46] a compound of the formula $3CaO.2Fe_2O_3$ could be formed at 1,450 deg. C. This has been shown to be a mixture of $2CaO.Fe_2O_3$ and $CaO.Fe_2O_3$. The same authors reported that the calcium ferrites were more stable towards water and dilute acids than were the corresponding silicates. Andersen[47] confirmed the work of Sosman and Merwin. Martin[48] prepared the two ferrites and studied their behaviour with various reagents. In a later paper[49] he reported several other compounds of calcium oxide with ferric oxide ; his criteria for the existence of these compounds, however, appear to be inadequate.

Monocalcium ferrite (% CaO = 25.92) is prepared by heating an equimolecular mixture of CaO and Fe_2O_3 at 1,100 deg. C. It melts with decomposition at 1,216 deg. C. and is insoluble in 0.5N.HCl but soluble in 0.8–2.0 N.HCl.[50] It is not acted upon by water.[50] Its optical properties are : uniaxial and optically negative. Its refractive indices (lithium light) are : $\epsilon = 2.345$, $\omega = 2.465$.

Dicalcium ferrite (% CaO = 41.18) is prepared by heating a mixture of five parts by weight of calcium oxide with one part of ferric oxide above 1,200 deg. C. The free calcium oxide in the product is extracted by a glycerine-alcoholic solution of ammonium acetate.[50] The compound melts with decomposition at 1,436 deg. C. and is soluble in 0.5 N.HCl. It is decomposed slowly by water, yielding calcium hydroxide. Its optical properties are : biaxial and it is optically positive. Refractive indices (lithium light) : $a = 2.200$, $\beta = 2.220$, $\gamma = 2.290$.

Ternary Systems

THE SYSTEM $CaO-MgO-SiO_2$.[51]—The most important compounds occurring in this system are Monticellite, $CaO.MgO.SiO_2$, and the compound $2CaO.MgO.2SiO_2$ which has optical properties practically identical with the mineral akermanite. A ternary compound $5CaO.2MgO.6SiO_2$, which decomposes at 1,365 deg. C., is also found. Wollastonite and pseudo-wollastonite form solid solutions with (a) diopside, (b) $2CaO.MgO.2SiO_2$, and (c) $5CaO.2MgO.6SiO_2$. Wollastonite-diopside solid solutions contain a maximum of 17 per cent. diopside. The 17 per cent. diopside solution is decomposed at 1,340 deg. C. Pseudo-wollastonite-diopside solid solutions contain a maximum of 10 per cent. diopside. The wollastonite-$2CaO.MgO.2SiO_2$ solid solutions, extend to a composition containing 60 to 70 per cent. $2CaO.MgO.2SiO_2$, while the pseudo-wollastonite solutions only contain up to 23 per cent. $2CaO.MgO.2SiO_2$.

THE SYSTEM $CaO-MgO-Al_2O_3$.—The details of this system have been reported by Rankin and Wright[52] and by Gillson and Warren.[53]

THE SYSTEM $MgO-Al_2O_3-SiO_2$.[54]—The following substances occur in this system : (1) Periclase (MgO), corundum (Al_2O_3) and tridymite and cristobalite (SiO_2) ; (2) clinoenstatite, $MgO.SiO_2$; (3) forsterite, $2MgO.SiO_2$; (4) spinel, $MgO.Al_2O_3$; (5) sillimanite ($Al_2O_3.SiO_2$) ; (6) ternary compound cordierite ($2MgO.2Al_2O_3.5SiO_2$)—this body dissociates at its melting point and exists in two forms, (a) μ-form (unstable) crystallising from glass at temperatures below

about 950 deg. C., and (b) stable α-modification formed at somewhat higher temperatures from the μ variety.

THE SYSTEM $CaO\text{-}Al_2O_3\text{-}SiO_2$.—This system, bearing intimately on the constitution of Portland cement clinker, has been referred to in a previous paper by the present authors.

THE SYSTEM $CaO\text{-}Fe_2O_3\text{-}SiO_2$.—Hansen and Bogue[55] studied only that portion of this system which contains compounds which might exist in Portland cement clinker. The presence of the compounds previously described in the binary systems was verified but no optical evidence was obtained to indicate the existence of any ternary compounds of $CaO\text{-}Fe_2O_3\text{-}SiO_2$ in the regions studied.

THE SYSTEM $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$.[56]—(1) *Ternary Compound.*—One ternary compound occurs with the formula $4CaO.Al_2O_3.Fe_2O_3$ and is called Brown-millerite. It melts congruently at $1,415 \pm 5$ deg. C. and is easily formed by heating a mixture of the finely powdered components in correct proportions. Density $= 3.77$.

OPTICAL PROPERTIES : Often occurs as prismatic grains with very small extinction angle against the prismatic faces ; occasional polysynthetic twinning. Optical character, negative. Optic axial angle, medium. Refractive indices— Lithium light : $\alpha = 1.96$, $\beta = 2.01$, $\gamma = 2.04$. Hg line ($\lambda = 578$) : $\alpha = 1.98$, $\beta = 2.05$, $\gamma = 2.08$ (± 0.01 in every case). Pleochroism : $\gamma =$ brown and $\alpha =$ yellow brown.

(2) Eutectic Mixtures.—(a) $4CaO.Al_2O_3.Fe_2O_3$ and CaO. Composition of eutectic mix $=$ CaO $= 56$ per cent., $Al_2O_3 = 17$ per cent. and $Fe_2O_3 = 27$ per cent. Melting point $= 1,395 \pm 5$ deg. C.

(b) $4CaO.Al_2O_3.Fe_2O_3$ and $5CaO.3Al_2O_3$. Composition of eutectic mix $=$ CaO $= 47$ per cent., $Al_2O_3 = 43$ per cent., $Fe_2O_3 = 10$ per cent. Melting point $= 1,335 \pm 5$ deg. C.

(3) Solid Solutions.—(a) $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$. Complete series of solid solutions. The solid solutions rich in $2CaO.Fe_2O_3$ are biaxial and optically positive ; those rich in $4CaO.Al_2O_3.Fe_2O_3$ are biaxial and optically negative.

(b) $CaO.Al_2O_3$ takes up about 15 per cent. of $CaO.Fe_2O_3$ in solid solution. The indices of refraction of $CaO.Al_2O_3$ then increase from $\alpha = 1.643$ and $\gamma = 1.663$ to about 1.70 for α and 1.72 for γ (sodium light).

(c) $CaO.Fe_2O_3$ takes up about 10 per cent. of $CaO.Al_2O_3$ in solid solution. The indices of refraction of $CaO.Fe_2O_3$ then decrease from $\omega = 2.465$ and $\epsilon = 2.345$ to about 2.25 for ω and 2.13 for ϵ (lithium light). The incongruent melting point of $CaO.Fe_2O_3$ (1,216 deg. C.) is also lowered to 1,205 deg. C. in taking up $CaO.Al_2O_3$ in solid solution. At this temperature this solid solution of $CaO.Al_2O_3$ in $CaO.Fe_2O_3$ dissociates into liquid and solid solution of $2CaO.Fe_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$.

COMBINATIONS OF Al_2O_3 AND Fe_2O_3 WITH CaO AND MgO.[57]—(1) Compounds. (a) $4CaO.2MgO.Al_2O_3.Fe_2O_3$.—This is prepared by heating the correct mix to 1,340 deg. C. ; specific gravity $= 3.72$. (b) $2CaO.MgO.Fe_2O_3$ is prepared by

heating the proper mixture at 1,300 deg. C., regrinding, and reheating ; it dissociates at 1,410 deg. C. $\pm$ 5 deg. C.   The optical properties are :

TABLE IV.

	$4CaO.2MgO.Al_2O_3.Fe_2O_3.$	$2CaO.MgO.Fe_2O_3.$
Optic axial angle	Uniaxial or biaxial with very small optic axial angle.	Biaxial with small optic axial angle.
Optical character	——	Positive.
Refractive Index .... (lithium light.)	$\alpha = 1.92$ $\gamma = 1.97$ $\pm$ 0.01	$\alpha = 2.13$ $\gamma = 2.28$ $\pm$ 0.01
Pleochroism	$\alpha =$ yellow brown. $\gamma =$ dark brown, almost opaque. Twinning is frequent.	$\alpha =$ dark brown, almost opaque. $\gamma =$ yellow brown.

(2) Solid Solutions.   (a) $4CaO.Al_2O_3.Fe_2O_3$ and MgO form a series of solid solutions until the composition $4CaO.2MgO.Al_2O_3.Fe_2O_3$ is reached ;   solid solutions in which the ratio of MgO to $4CaO.Al_2O_3.Fe_2O_3$ is greater than unity dissociate at 1,370 $\pm$ 5 deg. C. into MgO and liquid.   (b) $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$.   (c) $4CaO.2MgO.Al_2O_3.Fe_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$. (d) $4CaO.2MgO.Al_2O_3.Fe_2O_3$ and $2CaO.MgO.Fe_2O_3$.   (e) $4CaO.2MgO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$.   (f) $2CaO.MgO.Fe_2O_3$ and $2CaO.Fe_2O_3$.

(3) Replacements.—The alumina in the aluminates $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ can be partially replaced by ferric oxide.   Generally, ferric oxide is capable of replacing about 2 per cent. of alumina in the compounds $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$, and the indices of refraction are thereby raised from 1.710 $\pm$ 0.002 to 1.715 $\pm$ 0.003 and from 1.608 $\pm$ 0.002 to 1.613 $\pm$ 0.003 respectively. Probably in the case of aluminates separating as a primary phase from melts, changes in the composition occur during cooling, the amount of alumina replaced by ferric oxide being a function of the temperature and the concentration of ferric oxide in the melt.

REFERENCES.

[32] Baylis, *J. Phys. Chem.*, 32, 1236 (1928).
[33] Jolibois and Chassevent, *Compt. rendus.*, 188, 452 (1929).
[34] Rankin and Wright, *Am. J. Sci.*, 4th Series, 39, No. 229 (1915).
[35] Greig, *Am. J. Sci.*, 13, 1 (1927).
[36] Ferguson and Merwin, *Am. J. Sci.*, 48, 81 (1919).
[37] Nagai and Asaoka, *J. Soc. Chem. Ind. Japan*, 33, 315B (1930).
[38] Bates, *J. Amer. Cer. Soc.*, 1, 679 (1918).
[39] Bates, Tech. Paper 197, *U.S. Bur. Stds.* (1921).
[40] Bates and Klein, Tech. Paper 78, *U.S. Bur. Stds.*
[41] Stern, *Z. Anorg. Chem.*, 63, 160 (1910).
[42] Koyanagi, *Zement*, No. 4 (1931).
[43] Campbell, *J. Ind. & Eng. Chem.*, 9, 943 (1917).
[44] Nagai and Naito, *J. Soc. Chem. Ind. Japan*, 32, 221, 286, 295 (1929).
[45] Sosman and Merwin, *J. Wash. Acad. Sci.*, 6, 532 (1916).
[46] Hilpert and Kohlmeyer, *Ber.*, 42, 4581 (1910).
[47] Andersen, *Bull. Norwegian Geological Soc., Christiana*, No. 1 (1922).
[48] Martin, *3me. Congrès. Chimie Industriel*, 406 (1924).
[49] Martin, *Mon. Sci.*, 15, 97 (1925).
[50] Nagai and Asaoka, *J. Soc. Chem. Ind. Japan*, 33, 130B, 161B, 190B, 256B (1930).
[51] Ferguson and Merwin, *Am. J. Sci.*, 48, 165 (1919).

[52] Rankin and Merwin, *J. Amer. Chem. Soc.*, 38, 568 (1926).
[53] Gillson and Warren, *J. Amer. Ceram. Soc.*, 9 (12), 783 (1926).
[54] Rankin and Merwin, *Am. J. Sci.*, 45, 301 (1918).
[55] Hansen and Bogue, *J. Amer. Chem. Soc.*, 48, 1261 (1926).
[56] Hansen, Brownmiller and Bogue, *J. Amer. Chem. Soc.*, 50, 396 (1928).
[57] Hansen and Brownmiller, *Am. J. Sci.*, 15, 225 (1928).
[58] Le Chatelier, *Compt. rend.*, 13, 94 (1882).
[59] S. B. and W. B. Newberry, *J. So.. Chem. Ind.*, 16, 887 (1897).
[40] Richardson, *Cement*, 4 (1903), 276, 340, 422 ; 5 (1904), 40, 87, 91, 117, 201, 261, 313 ; 6 (1905), 18.
[41] Campbell, *J. Ind. & Eng. Chem.*, 6, 706 (1914).
[42] Michaelis, *J. Soc. Chem. Ind.*, 28, 836 (1909).
[43] Newberry, *J. Soc. Chem. Ind.*, 16, 887 (1897).
[44] Campbell, *J. Ind. & Eng. Chem.*, 7, 835 (1915) and *ibid.*, 11, 116 (1919).
[45] Shepherd and Rankin, *Am. J. Sci.*, 28, 293.
[46] Bowen and Andersen, *Am. J. Sci.*, 37, 487.

Magnesia and Unsoundness. By DR. K. BALTHASAR. *Tonind.-Zeit.*, 1934, No. 16.—High-magnesia cements usually fall to pieces at between three weeks and eight months according to the amount of magnesia present. This unsoundness is different from that due to "free lime" and is not discovered by the boiling test. Sound cements can, however, be prepared from raw materials high in magnesia if the percentage of iron oxide is adjusted to the correct figure (calcined pyrites is useful for this purpose if the iron content is too low). The amount of iron that must be present depends on the magnesia according to the formula

$$Fe_2O_3 = 2(1 + 0.1 \times MgO)$$

A cement with 7 per cent. MgO, requiring therefore 3.4 per cent. Fe_2O_3, was made and used in 1924 and the concrete made with it is still good. When this formula is taken to the limit, if only MgO and Fe_2O_3 are present, the material known as "sintermagnesit" which serves as a blast-furnace lining is obtained. This has been used for many years and the weathering is scarcely noticeable.

If a graph is made with Fe_2O_3 as ordinate and MgO as abscissa and two lines are drawn, one connecting the points (Fe_2O_3 2 per cent., MgO 0 per cent.) and (Fe_2O_3 18 per cent., MgO 82 per cent.) and the other connecting points (Fe_2O_3 0 per cent., MgO 0 per cent.) and (Fe_2O_3 9.0 per cent., MgO 90 per cent.), a diagram is obtained which can be used for judging the magnesia-soundness of a cement. All cements lying on the first line will be sound, those lying between the two lines are doubtful and may or may not break up after long periods, while those lying below the second line will be all unsound. Cements lying above the first line are in the region of the high-magnesia Ferrite-Portland cements.

High-magnesia cements of suitable composition are highly resistant to saline solutions, especially sea water.

Waste-Gas Temperatures of Rotary Kilns.—II.
By Dr.-Ing. Rudolf Frey.

Efficiency of the Kiln.

The kiln efficiency can be judged from a knowledge of the waste-gas temperature which, according to the calculation indicated, is recognised as necessary for the heat balance. Compared with the present calculations of efficiency on rotary kilns this judgment has the advantage of not being equivocal. From the calculations hitherto customary two efficiencies were derived, here designated " chemical efficiency " and " physical efficiency." The first was obtained from a comparison of the measured consumption of heat with the heat theoretically necessary for the chemical transformation of the material. In physical efficiency the heat expended for evaporating the water contained in the raw material is also taken into consideration.

The efficiency that can be computed from the knowledge of the necessary waste-gas temperature is here called " thermal efficiency," and is obtained from comparison of the heat supplied by the furnace with the heat utilised between the maximum temperature and the waste-gas temperature, i.e., by the calculation

$$\eta_{th} = \frac{G_R \cdot c_{pm}R \cdot t_{max} - G_R \cdot c_{pm}R \cdot t_g}{G_R \cdot c_{pm}R \cdot t_{max}} \qquad \qquad \qquad \qquad (10)$$

If the variation of the specific heats of the flue gas is neglected the simplified formula is obtained

$$\eta_{th} = \frac{t_{max} - t_y}{t_{max}} \qquad \qquad \qquad \qquad \qquad \qquad \qquad (10a)$$

In the following this form is used as the definition of the thermal efficiency.

The graphical determination of the waste-gas temperature has the further advantage that it also gives simultaneously the waste-gas temperature for a kiln without shell losses if the curve of the heat constantly required is intersected with the curve of heat of the flue gas. The following deals with a kiln which only differs from the ordinary kiln in the absence of shell losses, and which on account of the limited resistance of the lining operates with the same maximum combustion temperature and the same temperature of the secondary air. The efficiency of such a kiln is designated " η_{id}," and is computed also from the relationship of the temperatures.

From a comparison of these figures there is obtained by the calculation $\eta_g = \eta_{th}/\eta_{id}$, a third proportional number which is the quality coefficient of the kiln. These three figures provide possibilities of comparing various kilns and judging their heat economy value. They also prevent one getting a wrong idea of the possibilities of fuel economy on account of chemical or physical efficiency. The figures show clearly that the rotary kiln purely without interior fittings permits only relatively small savings, and that the various attempts to abandon the purely rotary kiln principle are justified. This point will be dealt with again later in this series of articles, when the various influences on which fuel consumption depends are examined. A practical example of the calculations

necessary for the determination of fuel consumption are made here following the determination of the waste-gas temperature and efficiency.

Example of Method of Determining the Exit-gas Temperature and Efficiency of a Rotary Kiln.

The cement slurry (temperature 30 deg. C.) with 37 per cent. of water and a chemical heat requirement of 412 kcal. per kg. clinker computed on the basis of the raw mix analysis, was burned in a kiln 3·3 metres in diameter by 80 metres long at a clinkering temperature of 1,400 deg. C. (see Fig. 1), driving out from the raw mix 0·54 kg. CO_2 and 0·89 kg. of water per kg. of clinker. It is assumed that the kiln has a capacity of 300 tons per twenty-four hours, i.e., 12,500 kg. per hour, and that it is provided with chains for a length of eight metres. It is further assumed that the fuel used is bituminous coal dust with a net calorific value of 6,600 kcal. per kg. The following are therefore the calculations for determining the waste-gas temperature.

(1).—DETERMINATION OF THE CURVE OF HEAT REQUIRED. — The heat constantly required by the kiln consists of

		kcal.
(a) The chemical requirement of heat 1·205 × 425–100	=	412
(b) The requirement to heat the raw mix to 950 deg. C. 1·54 × 0·21 (950–30)	=	298
(c) The requirement for further heating to 1,400 deg. C. 1·00 × 0·25 (1,400–950)	=	112
Constant requirement :	=	822

The outside surface of the kiln is $\pi \times 3\cdot3 \times 80 = 830 m^2$.

The shell losses are :

At a waste-gas temperature of (deg. C.)..	150	300	450	600	750
per square metre per hour Q_w (kcal)...	1,450	1,860	2,600	4,050	5,875
Therefore per kg. clinker q_w (kcal.) ..	97	124	174	271	393
The ordinates of the line of heat required are then (kcal.)	919	946	996	1,093	1,215

(2) DETERMINATION OF THE CURVE OF FLUE-GAS HEAT.—The interior surface of the kiln with a lining 17·5 cm. thick is

$$2\cdot95 \times \pi \times 80 \quad .. \quad .. \quad .. \quad = 742 \text{ sq. metres.}$$

The additional surface on account of the chains

$$= 2\cdot95 \times \pi \div 4\cdot8 \quad .. \quad .. \quad = 55 \text{ sq. metres.}$$

Total surface   ..   ..   = 797 sq. metres.

The maximum temperature of the flue gas is fixed at 2,100 deg. C.

The amount of flue gas per kg. of coal is, according to formula (7a), at an excess of air of 1·10   ..   ..   11·4 kg.

The heat content per kg. of flue gas without preheating is therefore 6,600 ÷ 11·4   ..   ..   ..   =   579 kcal.
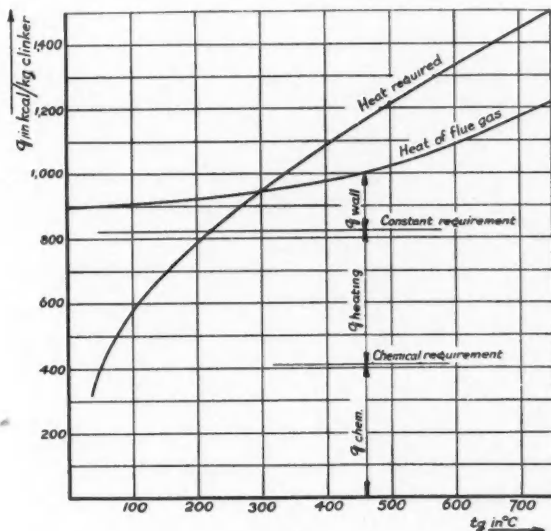
Fig. 7.

When 60 per cent. of the air is introduced as secondary air at 350 deg. C., then the heat content of this air per kg. coal is: $0.6 \times 10.4 \times 350 \times 0.242$ = 530 kcal.

and per kg. flue gas $530 \div 11.4$ = 47 kcal.

The entire heat content per kg. of flue gas therefore = 626 kcal.

This corresponds to a maximum temperature of the flue gas of 2,100 deg. C., and is therefore

$$t_{max} - t_s = \Theta_1 = 700 \text{ deg. C.}$$

For a waste-gas temperature of ..	150	300	450	600	750 deg. C.
The flue gas temperature is $t_g - t_e =$					
Θ_2 .. .. =	120	270	420	570	720 deg. C.
Therefore $\Theta_1 - \Theta_2$ =	580	430	280	130	20 deg. C.
$ln\ \Theta_1$ =	6.551	6.551	6.551	6.551	6.551 deg. C.
$ln\ \Theta_2$ =	4.787	5.598	6.040	6.346	6.579 deg. C.
$ln\ \Theta_1 - ln\ \Theta_2$ =	1.764	0.953	0.511	0.205	0.028 deg. C.
Therefore Θm =	329	452	548	634	714 deg. C.

The mean heat exchange figure is (according to Fig. 5) 33 kcal. per sq. metre $\times\ h\ \times$ deg. C. The ordinates of the curve of the heat of the flue gas are therefore

671   955   1,150   1,330   1,500 kcal.

The intersection of the curve of heat required and the curve of the heat of flue gas lies at 300 deg. C. temperature of waste gas. The shell loss is seen to be 124 kcal. per kg. clinker (Fig. 7).

The thermal efficiency of the kiln is, according to equation (10a)

$$(2,100 - 300) \div 2,100 = 85 \cdot 7 \text{ per cent.}$$

The waste-gas temperature of the kiln with perfect insulation would be 230 deg. C. and the efficiency $(2,100 - 220) \div 2,100 = 89 \cdot 5$ per cent.

The quality coefficient is therefore $85 \cdot 7 \div 89 \cdot 5 = 95 \cdot 8$ per cent.

Determination of Fuel Consumption.

The shortest way to determine the fuel consumption of a rotary kiln, when the waste-gas temperature and the shell loss on the rotary tube are known, is to use the combination of all amounts of heat entering or leaving the kiln without taking into consideration heat movements inside of the kiln.

There enter the kiln the heat content of the combustion gases at the theoretical combustion temperature and the heat content of the raw material.

The following heats leave the kiln : (1) The chemical requirement, as expressed earlier ; (2) the waste heat of the material burned ; (3) the heat content of the dry flue gases ; (4) (a) the heat content of the steam in the waste gases and (b) the heat content of additions to the waste gases (carbonic acid driven out in the manufacture of cement or the like) ; and (5) shell losses by radiation and convection. For covering items 1, 2, 4 and 5 there is available the heat content of the flue gases between the maximum temperature and the waste-gas temperature. To this is added the heat content of the raw material. Item 3 is equal to the heat content of the flue gases between the waste-gas temperature and zero ; this item is left out of the calculation for the present, and is determined only for the waste-gas temperature found (the sum of items 1, 2, 4 and 5) from which sum the heat content of the raw material is deducted. The difference obtained must then be equal to the heat content of the flue gases between the maximum temperature and the waste-gas temperature. If this difference is therefore divided by the heat content of 1 kg. of flue gas between these temperatures, there is obtained the amount of flue gas which is necessary for supplying the heat required. The amount of flue gas resulting from the combustion of 1 kg. of coal was computed in the determination of the curve of the flue-gas heat, so that the coal consumption and the heat consumption in kcal. per kg. of material burned can be computed directly from the necessary weight of the flue gas per kg. of material burned.

Of the values which have to be used in carrying through the calculation for a rotary cement kiln only brief remarks are necessary. The chemical requirement (item 1) was dealt with earlier. Item 2 (waste heat of the material burned) is the heat content of the clinker on leaving the kiln and having a temperature of 1,000 to 1,100 deg. C. This temperature depends so much on the running of the kiln that it can be assumed for the calculation. Leaving out of question exceptional cases such as where a kiln is wrongly dimensioned, the maintenance of an average temperature of 1,050 deg. C. may be expected.

For item 4a (the heat content of the steam in the waste gases) Mollier's equation $i_w = 595 + 0 \cdot 47t$ is used for the heat content of the carbonic acid from the raw mix and the specific heats from tables. In Fig. 8 the heat contents are given
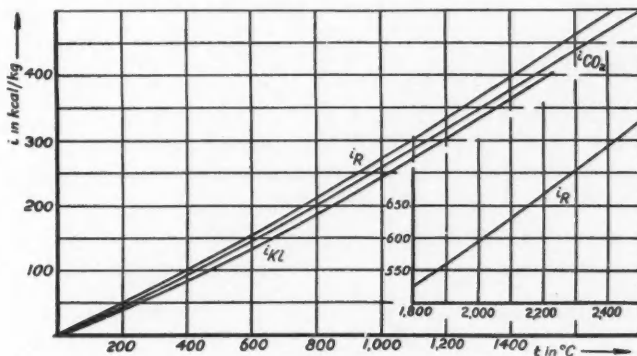
Fig. 8.

as curves as far as they are required here for the calculation, using as a basis the figures of Hartner for heat content of the cement clinker and those of Josse for the carbonic acid and the flue gases. The heat content of the raw material comprises that of the dry raw mix, whose specific heat is, according to Wecke, 0·21 kcal. per kg., and of the heat-content of the water content G_w; it is therefore

$$q_r = [(l + Gco_2) \cdot 0·21 + G_w].t_e \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \quad (11)$$

The following equation is therefore obtained for the calculation :

$$B \cdot G_R \cdot i_R = q_{chem} + c_{kl} \cdot t_{kl} + G_w \cdot i_w + Gco_2 \cdot ico_2 + q_{wall} - q_r \quad .. \quad (12)$$

Or, reduced according to B,

$$B = \frac{q_{chem} + c_{kl} \cdot t_{kl} + G_w \cdot i_w + Gco_2 \cdot ico_2 + q_{shell} - q_r}{(1 + 0.00157 \cdot H_u) \cdot (iRt_{max} - iRt_g)} \quad .. \quad (13)$$

The advantage of this calculation as compared with the usual calculation for heat balances from which the heat consumption is computed using an estimated waste-gas temperature and an assumed shell loss based on statistics, lies in the small number of the single items to be computed and, above all, in the fact that the processes in the interior of the kiln are entirely eliminated. The calculation contains nearly all the values necessary for setting up a diagram of the heat flow, so that these values need only be put together in the proper form.

The example given for the calculation of the waste-gas temperature is now continued. For the fuel consumption according to equation (13) is obtained

$$B = \frac{412 + 262 + 0·89 \times 736 + 0·54 \times 67 + 124 - 36}{11·35 \times (628 - 75)}$$

B = 2.63 ÷ 11.35 = 0.231 kg. per kg. clinker.

The balance necessary for setting up the diagram of the heat flow is :

Introduced into the Kiln :   kcal.

    1.—Through the kiln $2·63 \times 628 =$ 1,652
        i.e., in the fuel $0·231 \times 6,600 = 1,525$ kcal. ; with the
        primary air $2·40 \times 20 \times 0·241 \times 0·4 = 5$ kcal. ; with
        the secondary air $530 \times 0·231 = 122$ kcal.

    2. In the raw mix..   36

             Total   1,688
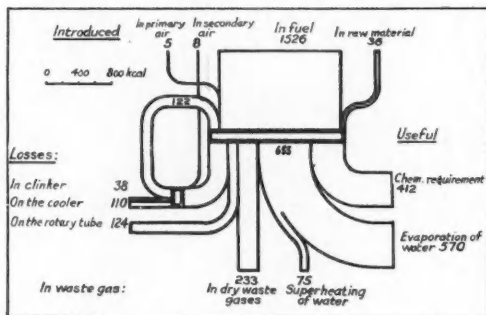
Fig. 9.

Leaving the Kiln :   kcal.

    1. Chemically consumed heat   412

    2. Waste heat of the clinker at 1,050 deg. C.   262

    3. In the combustion gases, $2 \cdot 63 \times 75 = 197$ kcal. In the carbonic acid of the raw mix, $0 \cdot 54 \times 67 = 36$ kcal.

In the dry waste gas :   233

    4. In the steam of the waste gases, $0 \cdot 89 \times 736 =$ 655

    5. Shell loss on the kiln   124

         Total   1,686

     The use of the heat contained in the clinker of 1,050 deg C. becomes clear from the following :

Introduced into the Cooler :

         kcal.

    1. In the clinker   262

    2. In the air   8

         Total   270

Discharged from the Cooler :

    1. In the preheated air   122

    2. In the clinker at 200 deg. C.   38

    3. Shell losses on the cooler   110

         Total   270

With these figures Fig. 9 is obtained.

Suggestions for Reducing Fuel Consumption.

     Being able from the preceding to calculate in advance the fuel consumption of a rotary kiln, two new questions arise : first, how can the reduction of the fuel consumption be devised from the calculation, and second, in what order may we place means for the reduction of the heat consumption, which is the most effective, and which do not pay for alterations ? From the heat calculations on rotary

kilns made up to the present the first question could be only partly answered, and the second not at all; it has therefore to be decided how the new calculation permits one to answer these questions.

(a) GENERAL RULES. The rules on which to work in the direction of a reduction of fuel consumption are obtained from a consideration of Fig. 7, wherein an example of the determination of waste-gas temperature is given. A lower fuel consumption due to a lower waste-gas temperature, that is to say smaller values of the co-ordinates of the point of intersection of Fig. 7, might be obtained either by lowering the curve of heat required or by making the curve of flue-gas heat steeper. An alteration of the curve of flue-gas heat is much more easily obtained because this is dependent on the constructional details and on the running of the kiln, while the curve of heat required is determined from the nature of the material burned and from the kiln lining, which can be altered only within narrow limits.

The possibility of making the curve of flue-gas heat steeper follows from its determinative equation

$$q = m \times \Theta_m \times F_i \div \text{capacity per hour.}$$

Accordingly q will be the greater, the greater are m, Θ_m and F_i and the smaller the capacity per hour.

It is well known that for a given rotary tube the fuel consumption per kg. of clinker may, on the one hand, be reduced by decreasing the capacity and, on the other hand, improved by improving the preheating, that is to say, by a higher maximum combustion temperature. The calculation also gives the means by which this can be attained, avoiding losses in the cooler and utilising as far as possible the entire heat of the clinker for preheating the secondary air, and using short pipelines for the fuel mixture so that a minimum of low temperature primary air is required. As already mentioned, for a coal consumption of less than 24 per cent., and fully using the heat of the clinker, it would still be possible to exceed the maximum temperature provisionally fixed at 2,200 deg. C., so that for these cases still more refractory lining would be required. But up to this limit there is still possible a further considerable saving of fuel with most kilns.

The influence of the interior surface F_i of the kiln is known, but it is mostly used only as a makeshift. It must be remembered that it is a question of increasing the interior surface of the kiln without increasing at the same time the outer surface. If this is done by increasing the length of the kiln, then the curve of heat required ascends and the effect of the alteration is reduced. Naturally, with unduly long rotary kilns lower waste-gas temperatures are obtained, but then the greater part of the heat so saved is lost from the kiln shell. Low consumption of coal is in this case obtained by a reduction of the capacity of the kiln per cubic metre of its contents. An alteration of the interior surface of the kiln without at the same time increasing the outer surface is possible only in two ways, (1) by building internal fittings, chains, and the like into the kiln, or (2) by using the kiln with its fixed relation of interior and exterior surface

for clinkering only, using for the preliminary treatment of the material a special apparatus having a large interior surface but a small radiating outer surface. This method has already been tried with success in the Lepol kiln for the dry process and in the Miag calcinator for the wet and dry processes.   By creating a large material surface very low waste-gas temperatures are obtained and at the same time shell losses are avoided by the use of good insulation.

With this division the efficiency of the remainder of the tube is at the same time increased so that, as already shown, with the higher feed temperature of the material the mean heat exchange coefficient m is also improved.   With the apparatus mentioned the feed temperature of the material may be as high as 300 to 400 deg. C. for the dry process, and the influence on the heat exchange coefficient, and with it indirectly on the efficiency of the rotary tube, can become very great.   In a lesser measure, however, the mean effective temperature difference becomes lower through the higher feed temperature of the material, but ultimately there is still an improvement of efficiency.

The mean temperature difference is also influenced by the height of the clinkering temperature.   Because its reduction also causes a decrease of the mean heat exchange coefficient, the position of the curve of the flue-gas heat is hardly improved by altering the clinkering temperature.   If this alteration of the clinkering temperature could be obtained it would change also the curve of heat required. On this line the influences are on the whole more difficult to ascertain.   On the first of the three items of which its ordinates consist (the requirement for the chemical transformation) practically nothing can be altered for a given example, and with the second item (the requirement for starting to heat the material) an alteration would only be possible by reducing the clinkering temperature.   This would still be perceptible with the third item (the shell losses), and the possibility of lowering the curve of heat required by means of additions or by greater fineness in the grinding of the raw material therefore deserves attention.

In connection with the shell losses, however, an attempt may be made to lower the heat requirement in connection with the thickness of the outer surface of the kiln and its capacity for heat radiation.   With the second factor there is the need already discovered of keeping as small as possible the relation of the outer surface of the kiln to the inner surface.   The consideration of the first factor, however, brings considerable difficulties in respect of construction and operation ; the problem of reducing the shell losses is nearly as old as the rotary kiln itself.

Other smaller influences on the heat consumption may consist in deviations from the normal through the formation of rings in the kiln, extensive presence of flue dust, and so on.   Their influence could not be traced by any calculation of test figures and they were therefore not taken into consideration in setting up the calculation.

(To be continued.)

Effect of Fluorides on Thermal Synthesis of Calcium Silicates.

By SHOICHIRO NAGAI and MAKIZO MIYASAKA.

THE following is an abstract of a report by Messrs. Shoichiro Nagai and Makizo Miyasaka, of the Institute of Silicate Industry, Tokyo Imperial University.

There are very few studies published on the effects of calcium fluoride and other fluorides on the thermal synthesis of calcium silicates. Some studies on this problem were reported by Erdmenger (*Tonindustrie-Zeitung*, 1882, 27) Kühl (*Zement*, 1924, 13, 3, 8, 18), Guttmann and Biehl (*Zement*, 1924, 13, 85), Becker (*Zement*, 1927, 16, 305), Jaenecke (*Zement*, 1932, 21, 377), etc. One of the present authors, S. Nagai, studied the thermal synthesis of calcium silicates ($3CaO.SiO_2$ $2CaO.SiO_2$ and $CaO.SiO_2$) in the presence of Al_2O_3, Fe_2O_3, Cr_2O_3, MgO, etc. (*Cement and Cement Manufacture*, October, 1933). The present studies deal with the effects of calcium fluoride (fluorspar) or other fluorine compounds on the thermal synthesis of these silicates.

The raw mixtures were made from the pure chemicals, calcium carbonate or calcium oxide, silicic acid anhydride, etc., in molecular ratio of (1) $CaCO_3.SiO_2$ (1 : 1) or $CaO.SiO_2$ (1 : 1), (2) $CaCO_3.SiO_2$ (2 : 1) or $CaO.SiO_2$ (2 : 1) and (3) $CaCO_3.SiO_2$ (3 : 1) or $CaO.SiO_2$ (3 : 1). These mixtures were heated, with or without calcium fluoride, in a tube furnace. The amount of calcium fluoride in the raw mixtures was 1 per cent. of the mixtures, and other percentages were sometimes compared. The heated products were tested systematically on the degree of combination, as follows : (1) Free lime or uncombined lime, (2) insoluble residue, or uncombined or free silica, (3) total lime, (4) total silica, (5) combined lime from (3) to (1) and its percentage, (6) combined silica from (4) to (2) and its percentage, (7) amount of synthesised calcium silicates, (8) molecular ratio of combined lime to combined silica or molecular ratio of lime to silica of the synthesised calcium silicates, (9) amount of calcium fluoride remaining in the heated product, (10) specific gravity of the heated product, etc.

On heating the mixture $CaCO_3.SiO_2$ (1 : 1) with and without 1 per cent. of calcium fluoride for one hour at temperatures from 800 to 1,300 deg. C. the presence of 1 per cent. of calcium fluoride had a decided effect on the formation of calcium silicates : (1) for the same degree of formation of calcium silicates, the addition of 1 per cent. calcium fluoride lowered the heating temperature by about 200 deg. C. ; (2) the combination of lime proceeds faster than that of silica. The molecular ratio of lime to silica becomes greater and reached nearly 2.0 at about 1,000 deg. C., so that the presence of fluoride has considerable effect in producing $2CaO.SiO_2$, even from the raw mixture of $CaCO_3.SiO_2$ (1 : 1) or $CaO.SiO_2$ (1 : 1).

In the case of the raw mixture from lime and silica, $CaO.SiO$ (1 : 1) and heating for one hour at temperatures of 700 to 1,000 deg. C., the effect of calcium fluoride is also very clear even at 700 to 800 deg. C.

By varying the heating time from half an hour to 1, 2 and 4 hours at 1,100 deg. C., with and without calcium fluoride, the combination between CaO and

SiO_2 was considerably promoted by the presence of 1 per cent. calcium fluoride. The molecular ratio of CaO to SiO_2 becomes smaller, showing the change of $2CaO.SiO_2$, which is produced at first by the shorter heating, to $3CaO.2SiO_2$ or $CaO.SiO_2$ of smaller molecular ratio of CaO to SiO_2.

Book Review.

Dust. By S. C. Blacktin. Pp. 296. (London : Chapman and Hall, Ltd., Price 18s. net.)

A VOLUME which is a co-ordination of the knowledge concerning dust has the advantage of putting the whole subject of dust production and dust occurrence in proper perspective. There is a tendency for residents in industrial areas—and among these the centres of cement manufacture are included—to believe that the dust arising from factories is the only form to be considered. To such it may come as a surprise to learn of the numerous other sources of dust and of the quantities that are in movement. The tails of comets, volcanoes, geological erosion, and vegetation all add their quota to the total dust content of the earth, or, as the author designates it, the staubosphere. Industrial dusts thus form the subject of only one chapter in this book, and cement works dust is dismissed in two or three sentences. One chapter is devoted to the pathological aspect of dust. Methods of dust measurement are described, but commercial methods of dust prevention and collection are very briefly considered. The greater part of the book deals with what might be classed as natural dusts, and there are comprehensive references to the literature of the subject.